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CHEMISTRY:

GENERAL, MEDICAL, AND PHARMACEUTICAL.

At the First International Pharmaceutical Exhibition, held in Vienna in August, 1883, *for this Manual the Author was awarded a Gold Medal.*

The Fourteenth and Fifteenth Editions of this Manual are adapted, respectively, to the Pharmacopœia of the United States and the British Pharmacopœia, and are produced concurrently.

CHEMISTRY:

GENERAL, MEDICAL, AND PHARMACEUTICAL:

INCLUDING

THE CHEMISTRY OF THE BRITISH PHARMACOPŒIA.

A MANUAL

ON THE GENERAL PRINCIPLES OF THE SCIENCE, AND THEIR
APPLICATIONS IN MEDICINE AND PHARMACY.

BY

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FIFTEENTH EDITION.

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MDCCCXCIII.

"But the greatest error of all is, mistaking the ultimate end of knowledge; for some men covet knowledge out of a natural curiosity and inquisitive temper: some to entertain the mind with variety and delight; some for ornament and reputation; some for victory and contention; many for lucre and a livelihood; and but few for employing the Divine gift of reason to the use and benefit of mankind."—LORD BACON.

"I hold that the greatest friend to man is labour; that knowledge without toil, if possible, were worthless; that toil in pursuit of knowledge is the best knowledge we can attain; that the continuous effort for fame is nobler than fame itself; that it is not wealth suddenly acquired which is deserving of homage, but the virtues which a man exercises in the slow pursuit of wealth; the abilities so called forth, the self-denials so imposed; in a word, that Labour and Patience are the true schoolmasters on earth."—LORD LYTTON.

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PREFACE.

THE short title on the back of a book, and even the words on the title-page, are generally, and even necessarily, imperfect descriptions of the contents, and hence not infrequently induce at the outset misconceptions in the minds of readers. The author of "Chemistry: General, Medical, and Pharmaceutical" would at once state, therefore, that his chief aim is to teach the general truths of chemistry to medical and pharmaceutical pupils. So far as laws and principles are concerned, the book is a work on General Chemistry; but inasmuch as those laws and principles are elucidated and illustrated by that large portion of chemistry which is directly interesting to medical practitioners and pharmacists, the book may be said to be a work on Medical Chemistry and on Pharmaceutical Chemistry. Only in this conventional sense would the author speak of Medical and Pharmaceutical Chemistry; for the truths of chemistry are the same for all students—crystalline verities which cannot be expanded or compressed to suit any class of workers. The leading principles of the science, however, can as easily be illustrated by or deduced from those facts which have interest as from those which have little or no special interest to the followers of medicine and pharmacy. The grand and simple leading truths or laws of chemistry, the lesser truths or principles, and nearly all the interesting relationships of elements and compounds, in a word, the *science* of chemistry, can be taught to medical and pharmaceutical students with little other aid than that afforded by the materials which lie in rich abundance all around these workers. Such a mode of teaching "the general principles of the science, and their applications in medicine and pharmacy," is adopted in this volume. It is a mode which greatly increases the usefulness of the science to the students chiefly addressed, while it in no way diminishes the value of chemistry to them as an instrument of mental culture—an instrument which sharpens and expands the powers of observation, which enlarges and strengthens memory and imagination, which gives point to the perceptive faculties, and which develops and elaborates the powers of thought and of reason.

This Manual is intended, then, as a systematic exponent of the general truths of chemistry, but is written mainly for the pupils, assistants, and principals engaged in medicine and pharmacy. It is essentially a Manual of Applied Chemistry, or Technical Chemistry, but is first of all a Manual of Chemistry.

The book will be found equally useful as a reading-book for students having no opportunities of attending lectures or performing experiments, or, on the other hand, as a text-book for college pupils; while its comprehensive Index, containing nearly ten thousand references, will fit the work for after-consultation in the course of business or professional practice.

From other chemical text-books it differs in three particulars:—first, in the exclusion of matter relating to compounds which at present are only of interest to the scientific chemist; secondly, in containing more or less of the chemistry of every substance recognised officially, or in general practice, as a remedial agent; thirdly, in the paragraphs being so cast that the volume may be used as a guide in studying the science experimentally.

The order of subjects is that which, in the author's opinion, best meets the requirements of medical and pharmaceutical students in Great Britain, Ireland, America, India, and the English Colonies. Introductory pages are devoted to a few leading properties of the elements. A review of the facts thus unfolded affords opportunity for stating the views of philosophers respecting the manner in which these elements influence each other as components of terrestrial matter. The consideration in detail of the relations of the elementary and compound radicals follows, synthetical and analytical bearings being pointed out, and attention frequently directed to connecting or underlying truths or general principles. The chemistry of substances met with in vegetables and animals, or of similar substances artificially produced (the so-called "organic chemistry") is next considered. Chemical toxicology and the chemical as well as microscopical characters of morbid urine, urinary sediments, and calculi are then given. The concluding sections form a laboratory-guide to beginners in the chemical and physical study of quantitative analysis. In the Appendix is a long table of tests for impurities in medicinal preparations, a short one of the saturating-powers of acids and alkalies designed for use in prescribing and dispensing, and an alphabetical list of elements and atomic weights.

In the course of the treatment outlined in the preceding paragraph, it will be observed that the whole of the elements are first noticed very shortly, to give the pupil a general view of his course of study, and afterwards at length and thoroughly; that the chemistry of the common metallic radicals precedes that of the rarer, and that the sections on the acidulous radicals are similarly divided; while the basylous radicals are arranged according to analytical relations, the common acidulous according to exchangeable value or quantivalence, and the rarer acidulous radicals alphabetically. By this plan the more important facts and principles are repeatedly brought under consideration, the points of view, however, differing according as interest is concentrated on physical, synthetical, analytical, or quantitative properties. This arrangement of matter was adopted, also, partly in the belief that the separate and general truths of chemistry never do or can enter the mind in the order of any scientific classification at present possible. Chemical facts are not yet united by any single, consistent theory. In the current state of chemical knowledge, consistency in the methodical arrangement even of elements can only be carried out in one direction, and is necessarily accompanied by inconsistencies in other directions—a result most perplexing to learners, and hence totally subversive of the chief advantage of classification. For this reason the writer has preferred to lead up to, rather than follow, scientific classification—has allowed analogies and affinities to suggest, rather than be suggested by, classification. Among the acidulous radicals, especially, any known system of classification would have given undue prominence to one set of relations, and undeserved obscurity to others. Then, by separating more important from less important matter, instruction is adapted to the wants of gentlemen whose opportunities of studying chemistry vary greatly, and are unavoidably insufficient to enable them to gain a knowledge of the whole area of the science. One great advantage of the mode of treatment is, that difficulties of nomenclature, notation, chemical constitution, and even those arising from conventionality of language, are explained as they arise, instead of being massed under the head of "Introductory Chapters," "Preliminary Considerations," or "General Remarks," which are not infrequently too difficult to be understood by a beginner, too voluminous to be remembered except by the aid of subsequent lessons, and are consequently the cause of much trouble and confusion. For an illustration of the treatment thus adopted by the author, the reader is referred to the various notes on chemical constitution—*see* "Constitution," "Structure," etc., in the Index. This plan has also admitted of greater prominence being given to "The General Principles of Chemical Philosophy," the only section to which the student is asked frequently to return until he finds himself naturally employing those principles in the interpretation of the phenomena obtained by experiment.

An elementary knowledge of the subjects of Gravitation, Heat, Light, Sound, Electricity, and Magnetism cannot be too strongly recommended to the student of chemistry. The first portion of this Manual would have been devoted to an exposition of these branches of physics, so far as they bear on chemistry, did not the many special books on physics render such a course unnecessary. Quantitative chemical analysis frequently involving determinations of temperature, specific gravity, and atmospheric pressure, a few paragraphs on these subjects are made introductory to the section on quantitative operations.

The theories that matter consists of molecules, and that molecules consist of atoms, are freely adopted in this book, the author believing that, in the present state of knowledge and education, philosophic conceptions concerning chemistry can only be induced in the minds of medical, pharmaceutical, and general students by the aid of those theories.

The chemical notation of the work is in accordance with modern views. Equations illustrative of pharmacopœial processes have, in all important cases, a name attached to each formula.

In the first edition of this Manual, in 1867, chemical nomenclature was modernized to the extent of defining the alkali-metal salts and the earthy compounds as those of potassium, sodium, ammonium, barium, calcium, magnesium, and aluminium, instead of potash, soda, ammonia, baryta, lime, magnesia, and alumina. The author confidently believes that this change, founded on views now adopted by all prominent writers on chemistry, will ultimately be accepted by all the various followers of medicine and pharmacy. It is a step in the direction of simplicity and consistency, and involves far less hypothesis than is contained in the old system. The name nitrate of potash, for example, was based on the pure assumption that nitre contained oxide of potassium or potash and nitric anhydride, then erroneously termed nitric acid. By the modern name, nitrate of potassium, all that is intended to be conveyed is, that nitre contains the element common to all potassium compounds, and the group of elements common to all nitrates. Under the old method, students always experienced difficulty in distinguishing salts of the metal from salts of its oxide—salts of potassium, for instance, from salts of potash; under the new view no such difficulty arises. Names such as potassium nitrate or potassic nitrate are also consistent with modern views, but for general adoption are too unlike the original. The contractions in Latin for names like "nitrate of potassium" are identical with the contractions for names resembling "nitrate of potash;" an accidental circumstance that will much facilitate the general introduction of the former names among the older medical practitioners and pharmacists, and a practical advantage that must determine the choice over the other chemically equivalent names just mentioned. The author ventures to express some gratification that his use and advocacy of this system from 1867 onwards resulted in its adoption, in 1873, in the "Pharmacopœia of the United States," and, in 1885, in the "British Pharmacopœia." Pharmacy amongst English-speaking nations will thus sooner or later, in the important matter of chemical nomenclature, be in accord with the teachings of chemical science.

The metric system of weights and measures (that which, doubtless, is destined to supersede all others) is alone used in the sections on quantitative analysis. In other parts of the Manual avoirdupois weights and imperial measures are employed, necessarily.

It is hoped that the numerous etymological references scattered throughout the following pages will be found useful. Words in Greek continue to be rendered, by special request, in English characters, letter for letter. The word "official" is used throughout for things recognised officially by the compilers of Pharmacopœias; "officinal," in its original application to the officina, or shop.

Students are strongly recommended to test their progress by frequent examination. To this end appropriate questions are appended to each subject.

The author's ideal of a manual of chemistry for medical and pharmaceutical students is one in which not only the *science* of chemistry is taught, but in which the chemistry of every substance having interest for the followers of medicine and pharmacy is noticed at more or less length in proportion to its importance, and at least its position in relation to the leading principles of chemistry set forth with all attainable exactness. The extent to which he has realized this ideal he leaves to others to decide. Such a work will doubtless in certain parts partake of the character of a dictionary; but this is by no means a fault, especially if a good index be appended; for the points of contact between pure and applied chemistry are thus multiplied, and abundant outlets supplied, by which a lover of the science may pass into other chemical domains by aid of other guides, or even into the regions of original research. Among the rarer alkaloids, bitter bodies, glucosides, salts of organic radicals, solid fats, fixed oils, volatile oils, resins, oleo-resins, gum-resins, balsams, and colouring-matters mentioned in this volume, will be found many such points whence the ardent student may start for the well-known, the less-known, or the untrodden paths of scientific chemistry.

Within twenty-six years a demand has arisen for fifteen large editions of this Manual. The First, in 1867, was intended as a handbook of practical chemistry only; but the notes and remarks made respecting most of the experiments were found to be so useful by students that this portion of the volume was in the Second Edition (1869) sufficiently extended to render the book more fairly complete in itself. It, and all subsequent editions, included the Chemistry of the British Pharmacopœia. In response to a call from professional friends in the United States in 1870, the work was revised by the author for the followers of Medicine and Pharmacy in America, the Chemistry of the Preparations and Materia Medica of the United States Pharmacopœia being introduced, while those specially British were omitted, and such other adaptations were included as to form a Third Edition. A Fourth was presented to English workers in 1872, and, founded on the fourth, a Fifth Edition for American students in 1873. A very large Sixth Edition was published in England in 1875, and in America a Seventh in 1876 and an Eighth in 1879, the Sixth and all following Editions containing notices of substances official in the Indian Pharmacopœia. The Ninth, 1881, was an English Edition; the Tenth, 1883, an American; the Eleventh, 1885, English; the Twelfth, 1889, American; the Thirteenth, 1889, English; the Fourteenth, American.

The present, Fifteenth, Edition contains such alterations and additions as seemed necessary for the demonstration of the latest developments of chemical principles and the latest applications of chemistry to pharmacy. Hence, even if compared with the preceding English edition, on nearly every page will be found some indication of the recent rapid growth of the science and the art of chemistry. On the other hand, synthetical and analytical processes which have become more or less superseded have been either omitted or described less fully. The whole work has thus been kept within the limits of a learner's manual, while the author has endeavoured faithfully to portray the present relationship of chemistry to at least those areas of medicine and pharmacy with which students should become familiar in the days of their studentship. The voluminous Index will maintain the usefulness of the book to them afterwards in the course of the practice of their respective callings.

The author is indebted to his assistants, Mr. Frederick William Short, B. Sc. Lond., and Mr. Eustace Harold Gane, and to his son Dr. D. Harvey Attfield, M.A., D.P.H., Cantab., for much valuable help in preparing this edition for the press.

17, BLOOMSBURY SQUARE, LONDON,
October 2nd, 1893.

ADVICE TO STUDENTS

RESPECTING THEIR OBJECT IN STUDYING.

It is unnecessary to advise you to avoid studying chemistry, or indeed any subject, *merely* by way of "preparation for examination." You will not so mistake the means for the end. You are studying to fit yourself for your position in the world. Work diligently, study thoughtfully and deliberately; above all, be thorough; otherwise your knowledge will be inaccurate and transient, and will be unaccompanied by that enlightenment of the understanding, that mental training, mental discipline, and general elevation of the intellect which constitute, in a word, education. When you are thus educated, you will with ease and pleasure pass any examination in the knowledge you have thus acquired.

All authorities on education, whether statesmen, teachers, or examiners, regard "Examination," even by the most highly skilled "Board," with ample time at its disposal and a wide area from which to select questions, as but a partial test of knowledge, and an imperfect test of education. It is the least unsatisfactory, however, that has been devised, and is especially useful when, following instead of leading education, it is restricted to the subjects of a well-defined, earnestly followed, compulsory public curriculum of study—a curriculum directed by a competent representative body, administered by properly qualified teachers, and followed by pupils who have had sound preliminary training.

Students! in all honour and in the highest self-interest, take care that any inefficiencies inseparable from "examination" are abundantly compensated by the extent and precision of your knowledge, and by the soundness and thoroughness of your whole education.

APPARATUS.

LIST OF APPARATUS FOR EXPERIMENTS IN ANALYSIS.

List of Apparatus suitable for the three months' course of practical chemistry in the summer session of medical schools, or for any similar series of lessons—including the preparation of elementary gases, analytical reactions of common metals and acidulous radicals, analysis of single salts, chemical toxicology, and the examination of urine, urinary sediments, and calculi :—

One dozen test-tubes.
Test-tube stand.
Test-tube cleaning-brush.
A few pieces of glass tubing, 8 to 16 in. long, with a few inches of india-rubber tubing to fit.
Small flask.
Two small beakers.
Two small funnels.
Two watch glasses.
Two or three glass rods.
Wash-bottle.
Small pestle and mortar.
A 2-pint earthenware basin.
A 2-inch and a 3-inch evap. basin.
Two porcelain crucibles.
Blowpipe.
Crucible tongs.
Round file.
Triangular file.
Small retort-stand.
Sand-tray.
Wire triangles.
Platinum wire and foil.
Test-papers.
Filter-paper.
Towel.
Two dozen corks.

(*This set, packed in a case, can be obtained of any chemical-apparatus maker for* 12*s*. 6*d*. *to* 15*s*.)

LIST OF APPARATUS FOR EXPERIMENTS IN SYNTHESIS AND ANALYSIS.

A larger set, suitable for the performance of most of the synthetical as well as qualitative analytical experiments described in this manual :—

A set of evaporating-basins, of the following sizes :—
  One 8½-inch.
  One 7½-inch.
  One 6½-inch.
  One 4-inch.
  Two 3-inch.
One retort-stand and three rings.
Two test-glasses.
One half-pint flask.
Half a quire of filter-paper.
Two porcelain crucibles.
One measure-glass, 5 oz.
Blowpipe, 8-inch.
Two glass funnels.
One doz. test-tubes (hard glass).
One test-tube brush.
One pair of 8-inch brass crucible tongs.
Two soup-plates.
One flat-plate.
Two spatula knives.
One pair of scissors.
One round file.
One triangular file.
Half a pound of glass rod.
Half a pound of glass-tubing.
One foot of small india-rubber tubing.
Three dozen corks of various sizes.
Platinum wire and foil.
Test-papers.
A nest of three beakers.

(*This set, packed in a case, can be obtained of any chemical-apparatus maker for* 25*s*. *to* 30*s*.)

A sponge, towels, and a note-book may be included.

LIST OF FURNITURE OF A CHEMICAL LABORATORY.

The following apparatus should be ready to hand for students following an extended course of practical chemistry, in a room set apart for the purpose :—

A bench or table and stool.
Water-supply and waste-pipe.
A cupboard attached to a chimney with an outward draught.
A furnace fed with coke; tongs, hot-plate or sand-bath, etc.
A waste-box.
Shelves for chemical and other materials in jars or bottles.
Gas-supply and lamp with flexible tube (or a spirit-lamp and spirit).
Test-tube rack, two dozen holes.
Iron stand or cylinder for supporting large dishes.
Iron adaptors for fitting dishes to cylinder.
Pestle and mortar, 5 or 6 inches.
One 6-inch funnel.
Brown pan, 1 or 2-gallon.
White jug, 1-gallon.
Water-bottle, quart.
Twenty-eight test-bottles, 6 oz.

Other articles, such as flasks, retorts, receivers, condensers, large evaporating-dishes, may be obtained as wanted. In Quantitative Analysis the apparatus described in the sections on that subject will be required.

LIST OF FLUID REAGENTS.

Certain chemical substances are used so frequently in analytical processes that it is desirable to have small quantities placed in bottles in front of the operator (*see* page 7). As these reagents are generally employed in a state of solution, nearly all the solid salts may at once be dissolved (in distilled water). The bottles employed should be well stoppered, and of 5 or 6 ounces capacity. Common glass bottles of this size may be had for about four shillings per dozen. The bottles should not be more than about three-quarters full; single drops, if required, can then be poured out with ease and precision. The following list of test-solutions is recommended; directions for methods of preparing the substances not readily purchasable will be found by referring to the Index :—

Sulphuric Acid, strong.
Nitric Acid, strong.
Hydrochloric Acid, strong.
Acetic Acid, strong.
Sol. of Potash, 5 per cent. or B.P.
,, Soda, 5 to 15 per cent.
,, Ammon., 10 per cent. or B.P.
Lime-water, saturated.

The next nine may contain about 10 per cent. of solid salt :—

Carbonate of Ammonium, with a little solution of Ammonia added.
Chloride of Ammonium.
Phosphate or Arseniate of Ammonium.
Sulphydrate of Ammonium.
Chloride of Barium.
Chloride of Calcium.
Phosphate of Sodium.
Neutral Chromate.

The succeeding seven may have a strength of about 5 per cent. :—

Ferrocyanide of Potassium.
Ferricyanide of Potassium.
Iodide of Potassium.
Oxalate of Ammonium.
Perchloride of Iron.
Nitrate of Silver.
Perchloride of Platinum.

LISTS OF SOLID CHEMICAL SUBSTANCES FOR STUDY.

List of chemical substances necessary for the practical study of the non-metallic elements mentioned on pp. 1 to 23. The quantities are sufficient for several experiments.

Chlorate of Potassium	1 oz.	Phosphorus	½ oz.
Black Oxide of Manganese	1 oz.	Hydrochloric Acid	1 oz.
Zinc	1 oz.	Sulphur	½ oz.
Oil of Vitriol	2 oz.	Iodine	¼ oz.

List of chemical substances necessary for the *analytical* study of the important metallic and acidulous radicals (pp. 63 to 451). The quantities will depend on the frequency with which experiments are repeated or analyses performed ; those mentioned are sufficient for one or two students. The articles are given in the order in which they will be required. The eight substances mentioned in the above list are included.

The set of test-solutions described in the previous section.

Carbonate of Potassium	1 oz.
Tartaric Acid	1 oz.
Litmus	¼ oz.
Sulphate of Magnesium	1 oz.
Sulphate of Zinc	1 oz.
Alum	1 oz.
Sulphide of Iron	1 lb.
Oak-galls	1 oz.
Sulphocyanate of Potassium	¼ oz.
White Arsenic	½ oz.
Zinc	½ lb.
Charcoal	½ lb.
Sulphate of Iron	1 oz.
Copper Foil	1 oz.
Sulphate of Copper	1 oz.
Tartar Emetic	½ oz.
Mercury	1 oz.
Corrosive Sublimate	½ oz.

Calomel	½ oz.
Tin	1 oz.
Bicarbonate of Potassium	1 oz.
Acetate of Lead	1 oz.
Cyanide of Potassium	½ oz.
Hyposulphite of Sodium	1 oz.
A Lithium Salt	10 grs.
Nitrate of Strontium	¼ oz.
Black Oxide of Manganese	½ lb.
Chloride of Manganese	¼ oz.
Chloride of Cobalt	50 grs.
Nitrate of Nickel	¼ oz.
Chloride of Chromium	¼ oz.
Gold leaves	2 or 3.
Chloride of Cadmium	¼ oz.
Nitrate of Bismuth	¼ oz.
Bromide of Potassium	¼ oz.
Starch	1 oz.
Nitrate of Potassium	1 oz.
Copper borings or turnings	1 oz.
Indigo	¼ oz.

Chlorate of Potassium	1 oz.	Borax	1 oz.
Iodine	½ oz.	Turmeric	¼ oz.
Spirit of Wine	1 oz.	Benzoic Acid	50 grs.
Sulphur	1 oz.	Fluor Spar	1 oz.
Acid Oxalate of Potassium.	1 oz.	Tannic Acid	50 grs.
Citric Acid	1 oz.	Gallic Acid	50 grs.
Phosphorus	1 oz.	Pyrogallic Acid	50 grs.

The quantities of materials required for the study of chemistry *synthetically* will necessarily vary with the desires and tastes of the operator, or according to the number and requirements of students working together.

The materials that will be needed for the home-study of *organic chemistry* will vary with the requirements of the student. By the time he has qualified himself for a preliminary experimental course in that section of the science he may trust largely to his own judgment as regards both materials and apparatus.

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CHEMISTRY:

GENERAL, MEDICAL, AND PHARMACEUTICAL.

INTRODUCTION.*

MAN can neither create matter nor destroy matter, he can only alter its form—alter the relation of its elements to each other, or note similar alterations proceeding within and around him in Nature. To study those alterations, in all their known length and breadth and depth, is to study *Chemistry*.

The infinite varieties of solid, liquid, and gaseous matter of which our earth and atmosphere are composed may be resolved, with more or less difficulty, into a very few distinct substances appropriately termed Elements, for by no known means can they be further decomposed. About seventy of these Elements have been proved to exist. Some (such as gold) occur naturally in the uncombined state; but the greater number are combined in so subtle a manner as to conceal them from ordinary methods of observation. Thus none of the common properties of water indicate that it is composed of two elements, both gases, but differing much from each other: nor can the senses of sight, touch, and taste, or other common means of examination, detect in their concealment the three elements of which sugar is composed. The art by which these and all other compound substances are resolved into their elements is termed Chemistry, a name derived possibly from the Arabic word *kamai*, to conceal.* The *art* of Chemistry also includes the construction of compounds from elements, and the conversion of substances of one character into those of another. The general principles or leading truths relating to the elements, to the manner in which they severally combine, and to their properties when combined, that is, to the properties of the compound substances formed by their union, constitute the *science* of Chemistry.†

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* Students using this book as a guide in following chemistry practically, should read the first four pages, and then commence work by preparing oxygen. All students should read the prefatory pages, especially the page of "Advice to Students."

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* The idea that common metals contained valuable metals concealed within them was the one seed from which mainly sprung chemical knowledge. The men who endeavoured to find the secret of such concealment were appropriately termed *alchemists*, and their efforts spoken of as *alchemy* (*al kimia*, from *kamai*, to conceal). Their persistent labours, generation after generation, were unsuccessful so far as the transmutation of baser metals into gold was concerned, yet were invaluable to posterity; for new substances were discovered and truths of nature unveiled: from these discoveries multiplication of discoveries resulted, and thus grew the still growing branch of knowledge called Chemistry.

† Persons who practise the art and science of Chemistry are known as Chemists. Some two hundred or more years ago, and before Chemistry was a science, the only "Chemists" were the makers and vendors of chemical substances, then only used as medicines. They were the successors of the Alchemists. In Great Britain these chemists and the herb-dealers, otherwise drug-grocers, otherwise drug-gists, gradually associated to form the "Chemist and Druggist." Between the "Chemist and Druggist" and the Physician there existed the Apothecary—the putter together of medicines, or compounder of physicians' prescriptions. The Apothecary has since become a medical practitioner, prescriptions being now "made up" by the Chemist and Druggist. The latter in Great Britain, since the year 1868, has the *title* of *Chemist and Druggist*, his higher title being *Pharmaceutical Chemist;* these respective designations he legally assumes on passing the Minor and Major Examinations conducted by the Pharmaceutical Society of Great Britain, in accordance with the provisions of the Pharmacy Acts of 1852 and 1868. The whole class is often spoken of as that of *Pharmacists* or *Pharmaceutists*, terms also used in the United States. Other classes of Chemists are the Analytical Chemists, who give special attention to analysis; Manufacturing Chemists, who restrict their labours to the preparation of chemical substances; while others devote a portion of their knowledge and energies to Chemical Education or to Chemical Research, or are appealed to as Consulting Chemists by the persons, firms, corporations, or governments needing chemical advice respecting industrial processes, hygienic matters, etc. The callings of the Consulting and Analytical Chemist are generally united; and the professional gentlemen who follow these conjoint avocations also not infrequently occupy professorial or other tutorial positions, sometimes adding to these labours more or less work at original chemical research. In England, Scotland, and Ireland, nearly all the

From these few words concerning the nature of the art and science of chemistry, it will be seen that in most of the occupations that engage the attention of man, Chemistry plays an important part—in few more so than in the practice of Therapeutics[*] and of Pharmacy.[†]

Air, water, food, drugs, and chemical substances, in short, all material things, are composed, as stated, of Elements. An intimate knowledge of the properties of the more important Elements, both in the free and in the combined state, and of the various substances they form when they have combined with each other, some knowledge or idea of the power or force (the chemical force or chemical affinity) by which the elements contained in the compounds are held together, and an application of such knowledge to Pharmacy and Medicine, must be the objects sought to be attained by the learner for whom especially this book has been written.

The Elements.—Of the seventy or so known elements, about forty are of medical or pharmaceutical interest; of these, two-thirds are metals, and one-third non-metals; the remainder[‡] are so seldom met with in Nature as to have received no practical application, either in Medicine, Art, or Manufacture. Before intimately studying the Elements, it is desirable to acquire some general notions concerning them:

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leading professional Chemists are Fellows of the Institute of Chemistry of Great Britain and Ireland.

[*] Therapeutics (θεραπευτικός, *therapeutikos*, from θεραπεύω, *therapeuō*, I nurse, serve, or cure) is that branch of medicine which treats of the application of remedies for diseases. The therapeutist also takes cognisance of *hygiene*—that department of medicine which respects the preservation of health—and of *dietetics*, the subject of diet or food. By *pharmacology* is understood the normal action of drugs upon the system, as underlying the therapeutic action.—*Physics*, see p. 38.

[†] Pharmacy (from φάρμακον. *pharmakon*, a drug) is the generic name for the operations of preparing or compounding medicines, whether performed by the Medical Practitioner or by the Chemist and Druggist. It is also sometimes applied, like the corresponding term Surgery, to the apartment in which the operations are conducted. *Pharmacognosy* is the study of the crude drugs of the vegetable and animal kingdom.

[‡] A list of the elements will be found at the end of the Volume.

such a procedure will also serve to introduce the practical student to his apparatus, and make him better acquainted with the various methods of manipulation.*

Metallic Elements.—With regard to the metallic elements, it may safely be assumed that the reader has sufficient knowledge for present purposes; but little, therefore, need now be said respecting them. He has an idea of the appearance, relative weight, hardness, etc., of such metals as gold, silver, copper, lead, tin, zinc, and iron. If he has not a similar knowledge of mercury, antimony, arsenium, platinum, nickel, aluminium, magnesium, potassium, and sodium, he should embrace the earliest opportunity of seeing and handling specimens of each of these metals.

Non-Metallic Elements, wrongly termed Metalloids.—With regard to the non-metallic elements, it is here supposed that the student has no general knowledge. He should commence his studies, therefore, by a series of operations as follows, on eight of their number.

OXYGEN.

Preparation.—Oxygen is the most abundant element in nature, forming (in a state of combination) about one-half of the whole weight of our globe. To obtain it for experimental purposes all that is necessary is to apply heat—that force which will often be noticed as antagonistic, so to speak, to chemical union: heat generally separating particles of matter further from each other, while chemical attraction tends to bind them closer together—to heat certain compounds containing oxygen; the latter is then evolved in its normal, natural gaseous condition. Several substances, when heated, yield oxygen; but, for convenience of students, the crystalline body known as chlorate of potassium is best fitted for the experiment. The size and form of the vessel in which to heat it will mainly depend on the quantity required; but for the purposes of the student the best is a *test-tube*, an instrument in constant requisition in studying practical chemistry. It is simply a tube of thin glass, a few inches in length, and half or three-quarters of an inch in diameter, closed by fusion at one end. It is made of thin glass, in order that it may be rapidly heated or cooled without risk of fracture. (*See* figs. 3 and 4.)

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* This allusion to apparatus need not discourage the youngest pupil. With the aid of a few phials, wine-glasses, or other similar vessels, always at hand, he may, by studying the following pages, learn the chemical reactions which are constantly occurring in the course of making up medicine, understand the processes by which medicinal preparations are manufactured, and detect adulterations, impurities, or faults of manufacture. Among the substances used in medicine will be found nearly all the chemical materials required. If, in addition, a dozen test-tubes and a few feet of glass tubing be procured, many of the experiments described may be performed. For full lists of apparatus and chemical materials, see the introductory pages.

Outline of the Process.—Heat chlorate of potassium (say, as much as will lie on a shilling) in a test-tube, by means of a spirit, or gas-flame; gaseous oxygen is quickly evolved. Before applying heat, however, provision should be made for collecting the gas.

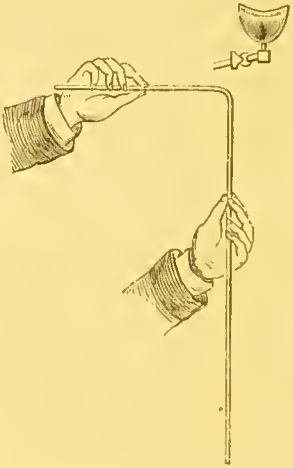
Collection of Gases (*see* fig. 3).—Procure a piece of glass tubing about the thickness of a quill pen, and a foot or eighteen inches long, and fit it to the test-tube by means of a cork, in the following manner. (Longer tubes may be neatly cut to any size by smartly drawing the edge of a triangular file across the glass at the required point, then clasping the tube, the scratch being between the hands, and pulling the portions asunder, force being exerted in a *slightly* curved direction, so as to open out the crack which the file has commenced.) The tube is fixed in the cork through a round hole made by the aid of a red-hot wire, or, better, by a rat-tail file, or, best of all, by one of a set of cork-borers—pieces of brass tubing sharpened at one end and having a flat head at the other. Fit the cork and test-tube to each other accurately and closely, but not so tightly as to break the test-tube. Setting aside the test-tube for a few minutes, proceed to bend the long piece of tubing to the most convenient shape for collecting the gas.

To Bend Glass Tubes.—Hold the part of the tube required to be bent in any gas- or spirit-flame (a fish-tail gas-jet, for example, fig. 1), constantly rotating it, so that about an inch of the glass becomes heated. It will soon be felt to soften, and will then, yielding to the *gentle* pressure of the fingers, assume any required angle. In the present case, the tube should be heated at about four inches from the extremity to which the cork is attached, and bent to an angle of 90 degrees (fig. 2).

Fig. 1.

SOFTENING AND BENDING GLASS TUBES.

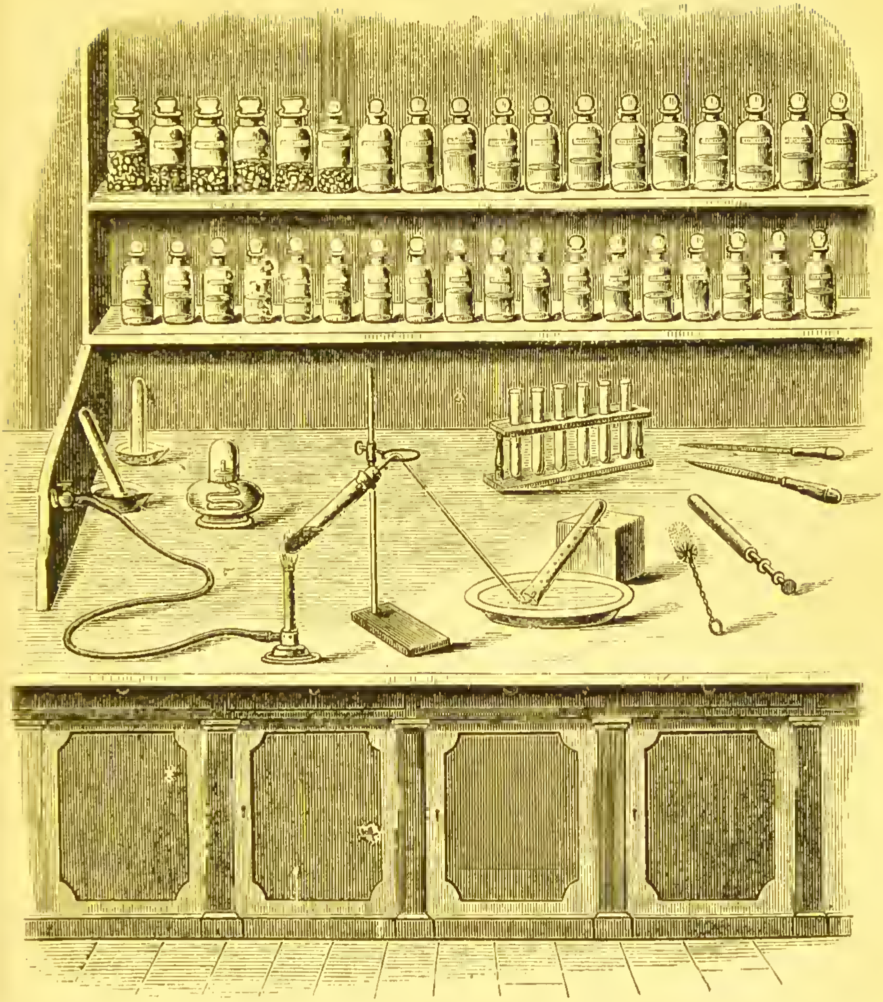
Fig. 2.



Source of Heat.—The source of heat for the test-tube may be the flame of an ordinary spirit-lamp, or, still better, where coal-gas is procurable, a mixture of the latter with air. Gas-lamps, especially constructed to burn a mixture of coal-gas and air, are sold by chemical apparatus manufacturers. (*See* figs. 3 and 7.)

Collection, etc. (continued).—Fit the cork and bent tube into the test-tube; the apparatus will then be ready for delivering gas at a convenient distance from the heated portion of the arrangement. To collect it, have ready three or four test-tubes (or small wide-mouthed bottles) filled with water, and inverted in a basin, or other vessel, also containing water, taking care to keep the mouths of the still full tubes a little below the surface. Now apply heat to the chlorate contained in the test-tube, and so arrange the open end of

Fig. 3.



This engraving represents the preparation, collection, and storage of small quantities of oxygen gas. A test-tube and bent glass tube, joined together by a perforated cork, are supported by the arm of an iron stand. (The apparatus might be held by the fingers). The tube is heated by a gas-lamp. (The spirit-lamp shown at back might be used instead.) Gas evolved from the heated substance in the test-tube is displacing water from an inverted test-tube. Spare tubes in a test-tube rack are at hand, and tubes already filled are set aside till wanted. A nest of cork-borers, a round file, a triangular file, and a test-tube cleaning brush are lying on the table or student's bench. Below are cupboards for apparatus, above are bottles containing testing liquids, etc.

the bent tube under the water that the gas which presently escapes with effervescence from the melted chlorate may pass out from the free end of the tube, and may bubble into and gradually fill the previously water-filled inverted test-tubes. The first tubeful may be rejected, as it probably consists of little more than the air originally in the apparatus, and which has been displaced by the oxygen. That which comes afterwards will be pure oxygen.

As each tube or bottle becomes full, close its mouth (still under the surface of the water) by a cork and then set it aside; or a little cup (such as a porcelain crucible or small gallipot) may be brought under the mouth, and the cup, with the mouth of the tube in it, be lifted out of the water and placed close by till wanted, the water remaining in the cup effectually preventing the gas from escaping.

On the large scale, oxygen may be made in the same way, larger vessels (glass flasks or iron bottles) being employed. Less heat also will be necessary if the chlorate of potassium be previously mixed with very fine sand, or, still better, with about an equal weight of common black oxide of manganese.

Note on the Collection and Storage of Gases.—It may be as well to state, that nearly all gases, whether for experimental or practical purposes, are collected and stored in a similar manner. Even coal-gas is generated at gas-works in iron retorts very much the shape of test-tubes, only they are as many feet long as a test-tube is inches; and the well-known gigantic gas-holders may be viewed as inverted iron test-tubes of great diameter.

Properties.—Free oxygen is a colourless gas. Cailletet and Pictet succeeded in liquefying it, and Wroblowski and Obszowski have obtained it in some amount as a definite, colourless, transparent fluid. Obviously it is not very soluble in water, or the gas could not be collected by the aid of that liquid. Oxygen is soluble to a certain extent, however (about 3 volumes in 100, at common temperatures), or fishes could not breathe. Other noticeable negative features are its want of taste and smell.

To show the relation of oxygen to combustion, remove one of the tubes from the water by placing the thumb over its mouth, and apply for a second a lighted wood match to the orifice; the gas will be found to be incombustible. Extinguish the flame of the match, and then quickly introduce the still incandescent carbonaceous extremity of the wood half-way down the test-tube; the wood will at once burst into flame, owing to the extreme violence with which oxygen gas supports combustion. These tests of the presence of free oxygen may also be applied at the extremity of the delivery-tube whilst the gas is being evolved. (It is desirable to retain two tubes of the gas for use in subsequent experiments; also one tube in which only one-third of the water has been displaced by oxygen.)

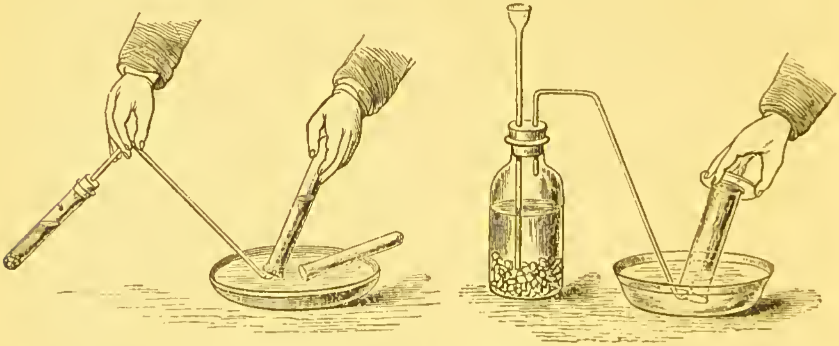
Relation of Oxygen to Animal and Vegetable Life.—Not only the carbon at the end of a piece of charred wood, but any other substance that will burn in air (which, as will be seen presently, is diluted oxygen) will burn more brilliantly in pure oxygen. The warmth of the bodies of animals is kept up by the continuous burning of the tissues in the oxygen (of the air) drawn into the system through the lungs. The product of this combustion is exhaled into the air as a gaseous compound of carbon and oxygen termed carbonic acid gas, a gas which, in sunlight, is absorbed by and decomposed in the cells of plants with fixation of the carbon and liberation of the oxygen; hence the atmosphere is kept constant in composition.

Memorandum.—At present it is not advisable that the reader should trouble himself with the consideration of the chemical action which occurs either in the elimination of oxygen from its compounds, or in the separation of any of the following non-metallic elements from their combinations. It is to the properties of those elements themselves, especially in their free and least active condition, that he should at present restrict his attention. Working thus from simple to more complex facts, he will in due time find that the comprehension of such actions as occur in the preparation of these few elements will be easier than if he attempted their full study now.

HYDROGEN.

Preparation and Collection.—The element Hydrogen is also, in the free state, a gas,* and is obtainable from its commonest compound, water, (of which one-ninth by weight is hydrogen), by the agency of hot zinc or iron, but more conveniently by the action of either of those metals on cold diluted sulphuric acid. The apparatus used for making oxygen may be employed for this experiment; but no lamp is required. Place several pieces of thin zinc † in the generating tube (fig. 4), or in any common glass bottle (fig. 5) or flask, and cover them with water. The collecting tubes

Fig. 4. *Fig.* 5.



PREPARATION OF HYDROGEN.

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* Graham obtained alloys of hydrogen with palladium and other metals, compounds in which several hundred times its bulk of gas is retained by the metal *in vacuo* or even at a red heat. This was physical confirmation of the opinion long held by chemists, that hydrogen is a gaseous metal. Graham termed it *hydrogenium*, other chemists *hydrium*, and considered its relative weight in the solid state to be nearly three-fourths that of water. Cailletet and Pictet have since actually liquefied and solidified this element.

† The best form is *granulated zinc* (*Zincum Granulatum*, B.P.), made by heating scraps of common sheet zinc in an iron ladle over a fire, and, immediately the metal is fused, pouring, in a slow stream, into a pail of water from a height of 8 or 10 feet. Each drop of zinc thus yields a thin little bell, which, for its weight, presents a large surface to the action of the acid liquid. If the zinc is allowed to become hotter than necessary, the little bells will not be formed. A trace of iron in the zinc greatly increases the rate at which the hydrogen is evolved.

(these also may be wide-mouthed bottles) being ready, add strong sulphuric acid (oil of vitriol) to the zinc and water, in the proportion of about 1 volume of acid to 5 of water, and fit on the delivery tube; or pour the acid down such a funnel-tube* as is shown in fig. 5; the hydrogen at once escapes with effervescence from the fluid. Having rejected the first portions (or having waited until the air originally in the bottle may be considered to be all expelled), collect four or five tubes of the gas in the manner described under Oxygen.

Notes.—This process is similar to that of the "British Pharmacopœia." In making larger quantities, bottles of appropriate size may be employed. Other metals, notably potassium and sodium, liberate hydrogen the moment they come into contact with water; but the processes are not economical, and the action is dangerously violent.

Properties.—Like oxygen, hydrogen gas is invisible, inodorous, and tasteless. If iron be used, the gas has a marked smell; but this is due to impurities derived from the iron.

Apply a flame to the mouth of the delivery-tube as soon as the operator's judgment tells him that the brisk effervescence of hydrogen must have resulted in the driving out of all air from the tube, for the *mixture* of hydrogen and air may explode. Ignition of the hydrogen gas ensues, showing that, unlike oxygen gas, it is combustible.

Plunge a lighted match well into a tube (or wide-mouthed bottle) containing free hydrogen; the gas is ignited, but the match becomes extinguished. This shows that hydrogen is not a supporter of combustion.

Hydrogen gas in burning unites with the oxygen of the air and forms water, which may be condensed on a cool glass or other surface. Prove this by holding a glass vessel a few inches above a hydrogen-flame. In burning the hydrogen contained in one of the tubes or bottles, the flamo is best seen when the tube is held mouth upwards, and water poured in so as to expel the gas gradually.

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* Funnel-tubes may be purchased of the apparatus-maker; or, if the pupil has access to a table blowpipe, and the advantage of a tutor to direct his operations, they may be made by himself.

If, instead of this gradual combination of the two elements oxygen and hydrogen, they be mixed together in bulk in the right proportions and then ignited, they will rapidly combine, and explosion will result. Prepare a mixture of this kind by filling up with hydrogen a test-tube from which one-third of the water has been expelled by oxygen. Remove the tube from the water, placing a finger over the mouth, and having a lighted match ready, apply the flame; explosion ensues, owing to the instantaneous combination of the whole bulk of the two elements, and the expansive force of the highly heated steam produced. If anything larger than a test-tube is employed in this experiment, it should be a soda-water bottle, or some such vessel equally strong.

Notes.—These gases thus unite at a temperature far higher than that of boiling water, two volumes of hydrogen and one of oxygen yielding two of gaseous water (true steam).

The noise of such explosions is caused by concussion between the suddenly expanded gaseous body and the air.

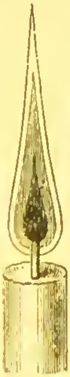
The force of the explosion, or, in other words, the force of the suddenly heated and therefore suddenly expanded steam, is below that necessary to break the test-tube. Some force, however, is exerted; and hence the necessity of the precaution previously suggested, of allowing all the air which may be in a hydrogen-apparatus to escape before proceeding with the experiments. If a flame be applied to the delivery-tube before all the air is expelled, the probable result will be ignition of the mixture of hydrogen and oxygen (of the air) and consequent explosion. But even in this case the generating vessel is not often fractured unless it be large and of thin glass, the ordinary effect being that the cork is blown out, and the delivery-tube broken on falling to the ground.

Hydrogen is a constituent of all the substances used for producing artificial light, such as solid fats, oil, and coal-gas. The explosive force of large quantities, such as a roomful, of coal-gas and air, though vastly below that of an equal weight of gunpowder, is well known to suffice for blowing out that side of the room which offers least resistance.

The composition of water can be proved analytically as well as synthetically, a current of electricity decomposing it, by "electrolysis" (λύω, *luo*, to decompose), into its constituent gases, twice as much hydrogen as oxygen, by volume, being produced.

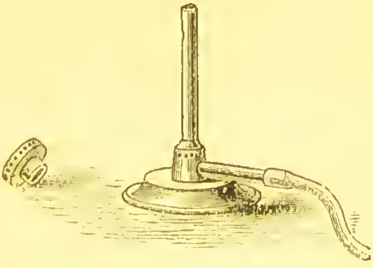
COMBUSTION (from *comburo*, to burn).—The experiments with hydrogen and oxygen illustrate the true character of combustion. Whenever chemical combination is sufficiently intense to be accompanied by heat and light, the materials are said to undergo combustion. Combustion only occurs at the line of contact of the combining bodies; a jet of oxygen will burn in an atmosphere of hydrogen quite as easily as a jet of hydrogen in oxygen. A jet of air (diluted oxygen) will burn as readily in a jar of coal-gas as a jet of coal-gas burns in air; each is combustible, each supports the combustion of the other. Hence the terms *combustible* and *supporter of combustion* are purely conventional, and only applicable so long as the circumstances under which they are applied remain the same. In the case of substances burning in air, the conditions are, practically always the same; hence no confusion arises from regarding air as the great supporter of combustion, and bodies which burn in it as being combustible.

Fig. 6.



STRUCTURE OF FLAME.

Fig. 7.



"BUNSEN," OR AIR-GAS, BURNER.

Structure of Flame.—A candle-flame (fig. 6) or oil-flame is a jet of gas intensely heated; the central portion is unburnt gas, the next envelope is formed of partially burnt and very dense gaseous and solid particles sufficiently highly heated to give light, and the outer cone of completely burnt gases. In the figure the sharpness of limit of these cones is purposely somewhat exaggerated. Air made by any mechanical contrivance, to mix with the gas in the interior of a flame at once burns up, or perhaps prevents the formation of, dense gases; giving a hotter, but non-luminous jet. The air-gas lamps (fig. 7), or "Bunsen" gas-burners, commonly used in chemical laboratories, are constructed on this principle: their flame has the additional advantage of not yielding a deposit of soot.

In the air-gas lamp coal-gas escaping from a small orifice draws rather more than twice its volume of air (supplied through adjacent holes) into its column; and the mixture of gas and air passes upwards along a pipe. It only burns at the end, and not within the pipe, partly because the metal of the burner, by conducting heat away, cools the mixture below the temperature at which it can ignite; partly because the velocity with which the mixture flows out is greater than the rate at which such a mixture ignites; and partly because the proportion of air to gas in the mixture is insufficient for perfect combustion, the external air contributing materially to the complete combustion of the jet of air-gas. The *Davy safety-lamp* acts on the principle first named: a wire-gauze cage surrounds an oil-flame; an inflammable mixture of gas (fire-damp) and air can pass through the gauze and catch fire and burn inside; but the flame cannot, ordinarily, be communicated to the mixture outside, because the metal of the gauze and of the other parts cools down the gas below the temperature at which combustion can continue.

Properties (continued).—Gaseous hydrogen is the lightest substance known. It was formerly used for filling balloons, but was superseded by coal-gas because coal-gas, though not lighter, is cheaper and more easily obtained. The lightness of hydrogen may be rendered evident by the following experiment:—Fill two test-tubes with the gas, and hold one with its mouth downwards and the other with its mouth upwards. The hydrogen will have escaped from the latter in a few seconds, whereas the former will still contain the gas after the lapse of many seconds. This may be proved by applying a lighted match to the mouths.

The relative weight or specific gravity of oxygen is sixteen times that of hydrogen. A vessel holding one grain of hydrogen will hold sixteen grains of oxygen. The relation of the weight of hydrogen to air is as 1 to 14·44, or as 0·0693 to 1·0. One grain of hydrogen by weight would measure about 27 fluid ounces, and, therefore, would about fill a common wine-bottle. Such a bottle would, at ordinary temperatures, hold about 14½ grains of air, or 16 grains of oxygen.

Mem.—It is desirable to retain two tubes of hydrogen for use in subsequent experiments.

Diffusion of Gases.—Hydrogen gas cannot be kept in such vessels as the inverted test-tube; for, though much lighter than air, it *diffuses* downwards into the air, while the air, though much heavier, diffuses upwards into the hydrogen. This power of *diffusion* is characteristic of all gases, and proceeds according to a fixed rate, namely, "in inverse proportion to the square root of the specific gravity of the gas" (*Graham*). Thus hydrogen diffuses four times faster than oxygen. This great and important property of diffusion strongly suggests that the particles of gases, at least, are always moving, never at rest; how otherwise *could* gases diffuse into each other as they do, notwithstanding the opposing influence of gravitation? Diffusion strongly supports this (Clausius's) kinetic (κινέω, *kineō*, to move, or put in motion) theory of the physical condition of gases.

PHOSPHORUS.

Appearance and Source.—Phosphorus (*Phosphorus*, B. P.) is a solid element, in appearance and consistence resembling white wax; but it gradually becomes yellow by exposure to light. It is a characteristic constituent of bones, and may be prepared from bones by a process which will be described subsequently.

Caution.—Phosphorus, on account of its great affinity for oxygen, takes fire very readily in the air, and should therefore be kept under water. When wanted for use, it must be cut under water. It is employed in tipping lucifers, though *red* or *amorphous phosphorus* (*vide* Index) is less objectionable for this purpose.

Experiment.—Dry a piece about one-fourth the size of a pea by quickly and carefully pressing it between the folds of porous (filter or blotting) paper; place it on a plate, and ignite by touching it with a piece of warm wire or wood. The product of combustion is a dense white suffocating smoke, which must be confined at once by placing an inverted tumbler, or beaker, or other similar vessel over the phosphorus. The fumes rapidly aggregate, and fall in white flakes on the plate. When this has taken place, and the phosphorus is no longer burning, moisten the powder with a drop or two of water, and observe that some of the water is converted into steam, an effect due to the intense affinity with which another portion of the water and the powder have combined, yielding heat.

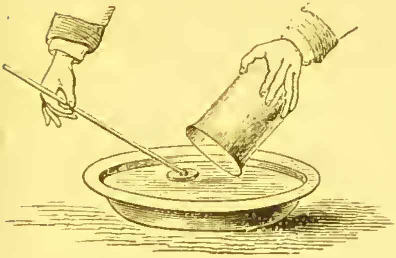
The powder produced by the combustion of phosphorus is termed phosphoric anhydride; the combination of the latter with the elements of water produces a variety of phosphoric acid which dissolves in the water, forming, on standing, a dilute solution of ordinary phosphoric acid. The Diluted Phosphoric Acid of the "British Pharmacopœia" is a similar solution, made in a somewhat different way, and of definite strength.

NITROGEN.

Source.—The chief source of this gaseous element is the atmosphere, nearly four-fifths of which consist of nitrogen (the remaining fifth being almost entirely oxygen).

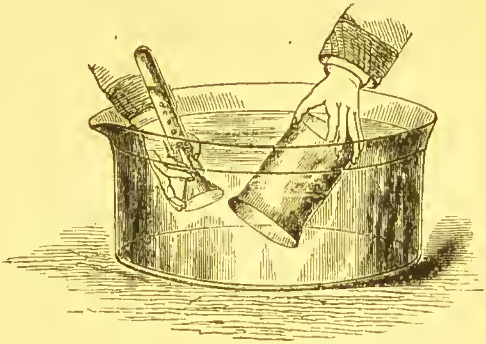
Preparation.—Burn a piece of dried phosphorus, the size of a pea, in a confined portion of air. The oxygen gas is thus removed, and the nitrogen gas remains. The readiest mode of performing this experiment is to fix a piece of earthenware (the lid of a small porcelain crucible answers very well) on a thin piece of cork, so that it may float in a dish of water (fig. 8). Place the phosphorus on the lid, ignite with a warm rod, and then invert a tumbler, or any glass vessel of about a half-pint capacity, over the burning phosphorus, so that the mouth of the glass may dip into the water. Let the arrangement rest for a short time, for the fumes of phosphoric anhydride to subside and dissolve in the water, and then decant the gas into test-tubes as indicated in fig. 9, using a tub or other vessel of water of sufficient depth to admit of the glass containing the nitrogen gas being turned on one side without air gaining access.

Fig. 8.



PREPARATION OF NITROGEN.

Fig. 9.



DECANTATION OF GASES.

Larger quantities of nitrogen gas are obtained in the same way. Other combustibles, as sulphur or a candle, might be used to burn out the oxygen gas from the air, but none answer so quickly and completely as phosphorus; added to which, the product of their combustion would not always be dissolved by water, but would remain with the nitrogen.

Mem.—The statement concerning the composition of the air is roughly confirmed in isolating nitrogen, about one-fifth of the volume of the air originally in the glass vessel having disappeared, its place being occupied by water.

Properties.—Like oxygen and hydrogen, nitrogen gas is invisible, tasteless, and inodorous. By pressure, Cailletet and Pictet condensed it to a liquid. Wroblewski and Obszewski obtained it in some amount as a definite, colourless, transparent fluid, which congeals, by its own evaporation, to a white snow-like solid. It is only slightly soluble in water. *Free* nitrogen is distinguished from all other gases by the absence of any very characteristic or positive properties. Apply a flame to some contained in a tube; it will be found to be incombustible. Immerse a lighted match in the gas; the flame is extinguished, showing that nitrogen is a non-supporter of combustion.

Nitrogen is fourteen times as heavy as hydrogen.

The chief office of the free nitrogen in the air is to dilute the energetic oxygen, a mere *mechanical* mixture resulting.

The air is nearly fourteen and a half (14·44) times as heavy as hydrogen. It may be liquefied and, apparently, solidified. Its average composition, including minor constituents (which will be referred to subsequently), is as follows:—

Composition of the Atmosphere.

	In 100 volumes.
Oxygen	20·61
Nitrogen	77·95
Carbonic acid gas	·04
Aqueous vapour	1·40
Nitric acid	traces
Ammonia	
Carburetted hydrogen	
Sulphuretted hydrogen	traces in towns.
Sulphurous acid	

Pure dry air free from carbonic acid *invariably* contains, by weight, 23 parts of oxygen to 77 of nitrogen; or, by volume, 20·76 parts of oxygen to 79·24 of nitrogen. Ozone (*vide* Index) is said to be a normal constituent of air.

Free Nitrogen and Combined Nitrogen.

The comparative inactivity or negative character of nitrogen in its free condition,—that is, when uncombined with other elements,—contrasts strongly with its apparent influence in a state of combination. When its compounds with hydrogen come to be studied, it will be found to be, apparently, the chief, or leading, or, in a sense, the most important element of those compounds—the ammoniacal compounds. United with carbon, it gives the poisonous cyanic substances. With oxygen, it yields quite a large group of bodies, amongst which are the common and important class of salts termed nitrates. With carbon as well as hydrogen and some oxygen, it affords powerful agents termed alkaloids—near relatives of ammonia; while the same elements otherwise grouped, and sometimes a little sulphur or phosphorus, form the various albumenoid and gelatinoid matters characteristic of the tissues of animals and vegetables. In a perfect structure we should perhaps scarcely regard any one element or member as more important than another, still such a conclusion almost forces itself upon us as we become acquainted with the chemical history of combined nitrogen. Free nitrogen is not, however, altogether inactive, for the nitrogen of the air appears to be absorbed and assimilated by plants—a given crop containing more nitrogen than the soil and manure whence it grew.

CHLORINE.

Source.—In the free state this element is a gas. Its chief source is common salt, more than half of which is chlorine.

Preparation.—About a quarter of an ounce of salt and the same amount of black oxide of manganese are mixed, and placed in a test-tube with sufficient water to cover them; on adding a small quantity of sulphuric acid, the evolution of chlorine gas commences. For the mode of collection see the following paragraphs.

Another process.—As the action of the sulphuric acid on the salt in the above process is mainly to give hydrochloric acid, the latter acid (about 4 parts) and the black oxide of manganese (about 1 part) may be used in making the gas, instead of salt, sulphuric acid, and black oxide of manganese. This, the usual process, is that adopted in the "British Pharmacopœia."

Collection and Properties.—Free chlorine is a suffocating gas. Care therefore must be observed in experimenting with this element. As soon as its penetrating odour indicates that it is escaping from the test-tube, the cork and delivery-tube (similar to that used in making oxygen) should be fitted on, and the gas passed to the bottom of another test-tube containing water (fig. 10). When thirty or forty small bubbles have passed, their evolution being assisted by slightly heating the generating tube, the latter should be removed to the cupboard usually provided in laboratories for performing operations with noxious gases or be dismounted and the contents carefully and rapidly washed away. The water in the collecting-tube will now be found to smell of the gas, chlorine being, in fact, soluble in about half its bulk of water. Chlorine-water is official * in the "British Pharmacopœia" (*Liquor Chlori*).

Fig. 10.

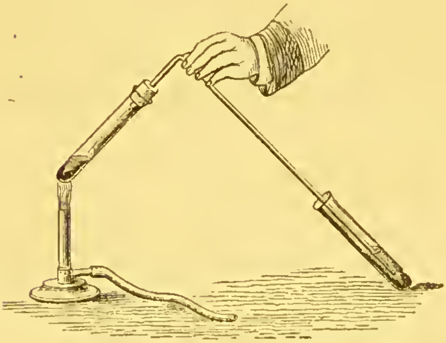
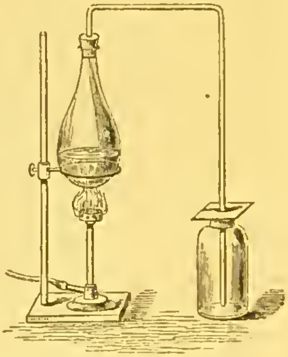


Fig. 11.



PREPARATION OF CHLORINE.

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* The Pharmacopœia and all in it is official (*office*, Fr. from L. *officium*, an office). There are many things which in pharmacy are officinal (Fr. from L. *officina*, a shop) but not official. To restrict the word *officinal* to the contents of a pharmacist's shop, and to that portion of the contents which is Pharmacopœial, is radically wrong, and should be avoided.

"An *official* formula is one given under authority. An *officinal* formula is one made in obedience to the customary usage of the shop (*officina*). To state that any preparation under the sanction of the British Pharmacopœia is officinal, is a misapprehension of the meaning of the word."—J. Brough.

"That is *official* which emanates from a recognised authority. That is *officinal* which is issued from an *officina* or workshop."—J. Ince.

"*Official* writings and orders are those issued by official persons. *Officinal* articles are such as are found in a shop." J. F. Stanford, M.A., F.R.S.

Larger quantities may be made from the hydrochloric acid and black oxide of manganese (4 to 1) in a Florence flask fitted with a delivery tube, the flask being supported over a flame by the ring of a retort-stand or any similar mechanical contrivance (fig. 11). A piece of cardboard on the neck of the collecting-bottle, as indicated in the figure, retards diffusion of the chlorine gas from the bottle during the process of collection.

Mem.—Flasks and similar glass vessels are less liable to fracture if protected from the direct action of the flame by being placed on a piece of wire gauze 2 to 4 inches square, or on a *sand-bath*, that is, a saucer-shaped tray of sheet iron on which a *thin* layer of sand is placed.

The *Vapor Chlori*, B.P., or Inhalation of Chlorine, is simply moist chlorinated lime so placed that some of the chlorine given off may be inhaled.

During these manipulations the operator will have noticed that chlorine is of a light yellowish-green colour. The tint is observable when the gas is collected in large vessels. As it is soluble in water (2⅓ vols. in 1 vol. at 60° F.), it cannot be economically stored over that liquid. Being, however, nearly twice and a half as heavy as air, the gas may be collected by simply allowing the delivery-tube to pass to the bottom of a dry test-tube or dry bottle (fig. 11).

A distinctive property of free chlorine is its bleaching-power. Prepare some coloured liquid by placing a few chips of logwood or other dyeing-material in a test-tube half full of hot water. Pour off some of this red infusion into another tube and add a few drops of the chlorine-water; the red colour is rapidly destroyed.

Free chlorine readily decomposes offensive effluvia; it is one of the most powerful of *deodorizers*. It also decomposes putrid and infectious matter; it is one of the best of *disinfectants*. (*Antiseptics* are substances which *prevent* putrefaction. *See* Index.)

Combination of Hydrogen with Chlorine, forming Hydrochloric Acid.—If an opportunity occurs of generating chlorine in a closed chamber or in the open air, a test-tube, of the same size as one of those in which hydrogen has been retained from a previous operation, is filled with the gas. The hydrogen-tube is then inverted over that containing the chlorine, the mouths being kept together by encircling them with a finger. After the gases have mixed, the mouths of the tubes are quickly in succession brought near a flame, when explosion occurs and fumes of a compound of hydrochloric acid gas with the moisture of the air are formed. The Hydrochloric Acid of pharmacy is a solution of the gas (made in a more economical way) in water.

The foregoing experiment affords evidence of the powerful affinity of chlorine and hydrogen for each other. Chlorine dissolved in water will, in sunlight, slowly remove hydrogen from some of the water and liberate oxygen. The bleaching-power of chlorine is generally referred to this indirect oxidizing effect which it produces in presence of water; for dry chlorine does not bleach.

Density.—Chlorine gas is $35\frac{1}{2}$ times as heavy as hydrogen gas. A wine-bottle would hold about $35\frac{1}{2}$ grains.

SULPHUR, CARBON, IODINE.

The physical properties (colour, hardness, weight, etc.) possessed by these elements, when they are in the free state, are familiar. Their leading chemical characters in the free state will also be understood when a few facts concerning each are made the subject of experiment.

SULPHUR.—Burn a small piece of sulphur; a penetrating odour is produced, due to the formation of a colourless gas. The product is a perfectly definite chemical compound of the oxygen from the air, with the sulphur. It is termed sulphurous anhydride, or sulphurous acid gas.

CARBON is familiar, in the free form, as soot, coke, charcoal, graphite (or plumbago, popularly termed blacklead), and diamond. The presence of combined carbon, in wood and in other vegetable and animal matter, is at once rendered evident by heat. Place a little tartaric acid on the end of a knife in a flame; the blackening that occurs is due to the separation of carbon. The black matter at the extremity of a piece of half-burned wood is also free carbon.

Carbon, like hydrogen, phosphorus, and sulphur, has a great affinity for oxygen at high temperatures. A striking evidence of that affinity is the evolution of sufficient heat to make the materials concerned red- or even white-hot. When ignited in the diluted oxygen of the air, carbon simply burns with a moderate glow, as seen in an ordinary coke or charcoal fire; but when ignited in pure oxygen, the intensity of its combination is greatly exalted. The product of the combination of the two elements, if the oxygen be in excess, is an invisible gaseous body termed carbonic acid gas; if the carbon be in excess, another invisible gas, termed carbonic oxide, results.

IODINE.—A prominent chemical characteristic of free iodine is its great affinity for metals. Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water and add a few iron filings or small nails. On gently warming this *mechanical* mixture, or even shaking if longer time be allowed, the colour and odour of the iodine disappear; it has *chemically* combined with the iron, a *chemical compound* has been produced. If the solution be filtered, a clear aqueous solution of the compound of the two elements is obtained.

This compound is an iodide of iron. Its solution, made as above, and mixed with sugar, forms, when of a certain strength, the ordinary Syrup of Iodide of Iron of pharmacy (*Syrupus Ferri Iodidi*, B.P.). A strong solution mixed with sugar and liquorice-root constitutes the corresponding Pill (*Pilula Ferri Iodidi*, B.P.). The solid iodide is obtained on removing the water of the above solution by evaporation.

Sulphur and *Iron*, also, when very strongly heated, *chemically combine* to form a substance which has none of the properties of a *mixture* of sulphur and iron—that is, has none of the characters of sulphur and none of iron, but new properties altogether. The product is termed Sulphide of Iron. Its manufacture and uses will be alluded to in treating of the compounds of iron; it is mentioned here as a simple but striking illustration of the difference between a *chemical compound* and a *mechanical mixture*.

THE ELEMENTS, THEIR SYMBOLS, ETC.

From the foregoing statements a general idea will have been obtained of the nature of several of the more frequently occurring free elements. Some additional facts concerning them may be gathered from the following Table, which gives the name in full, the symbol (or shorthand character *) of the name, and the origin of the name.

For the purposes of study by medical and pharmaceutical pupils, the elements may be divided into three classes, viz., those frequently, those seldom, and those never, used in pharmacy.

NAME.	SYMBOL.	DERIVATION OF NAME.
Oxygen . . .	O	From ὀξὺς (oxūs) *acid*, and γένεσις (genesis) *generation*, *i.e.* generator of acids. When first discovered it was supposed to enter into the composition of all acids.
Hydrogen . .	H	From ὕδωρ (hudōr) *water*, and γένεσις (genesis) *generation*, in allusion to the product of its combustion in air.
Nitrogen . .	N	From νίτρον (nitron), and γένεσις (genesis), *generator of nitre*.
Carbon . . .	C	From *carbo*, *coal*, which is chiefly carbon.
Chlorine . .	Cl	From χλωρὸς (chlōros) *green*, the colour of this element.
Iodine . . .	I	From ἴον (ion) *a violet*, and εἶδος (eidos) *likeness*, in reference to the colour of its vapour.
Sulphur . .	S	From *sal*, a *salt*, and πῦρ (pūr) *fire*, indicating its combustible qualities. Its common name, *brimstone*, has the same meaning, being the slightly altered Saxon word, *brynstone*, *i.e.* burnstone.
Phosphorus .	P	Φῶς (phōs) *light*, and φέρειν (pherein) *to bear*. The light it emits may be seen on exposing it in a dark room.

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* The symbol is also much more than the shorthand character, as will presently be apparent.

NAME.	SYMBOL.	DERIVATION OF NAME.
Potassium (Kalium)	K	*Kalium*, from *kali*, Arabic for *ashes* (see next paragraph). Manufactories in which compounds of potassium and allied sodium-salts are made, are called *alkali*-works to this day. *Potassium*, from *pot-ash;* so called because obtained by evaporating the lixivium of wood-ashes in pots.
Sodium (Natrium)	Na	*Natrium*, from *natron*, the old name for certain natural deposits of carbonate of sodium. *Sodium*, from *soda-ash* or *sodash*, the residue of the combustion of masses or *sods* of marine plants. Sod-ashes were chemically distinguished from pot-ashes by Duhamel in 1736. Previously both were simply *kali* or *ashes* from two different sources. Sir Humphry Davy first isolated the two metals, in 1807.
Ammonium	NH_4	This body is not an element; but its components exist in all ammoniacal salts, and apparently play the part of such elements as potassium and sodium. Sal ammoniac (chloride of ammonium) was first obtained from near the temple of Jupiter Ammon in Libya; hence the name.
Barium	Ba	From βαρὺς (barūs) *heavy*, in allusion to the high specific gravity of "heavy spar," the most common of the barium minerals.
Calcium	Ca	*Calx*, *lime*, the oxide of calcium.
Magnesium	Mg	From *Magnesia*, the name of the town (in Asia Minor) near which the substance now called "native carbonate of magnesium" was first discovered.
Iron (Ferrum)	Fe	Prehistoric. The spelling may be from the Saxon *iren*, the pronunciation from the Gothic "*iarn*." The derivation is perhaps Aryan; it probably originally meant *metal*.
Aluminium	Al	The metallic basis of alum was at first confounded with that of sulphate of iron, which was the alum of the Romans, and was so called in allusion to its tonic properties, from *alo*, *to nourish*.
Zinc	Zn	From Ger. *Zinn*, *tin*, with which Zinc seems at first to have been confounded.
Arsenium, Arsenicum, or Arsenic	As	'Αρσενικὸν (arsenikon), the Greek name for orpiment, a sulphide of arsenium. Common *white arsenic* is an oxide of arsenium.

NAME.	SYMBOL.	DERIVATION OF NAME.
Antimony . . (Stibium)	Sb	Στίβι (stibi), or στίμμι (stimmi) was the Greek name for the native sulphide of antimony. The word *antimony* is said to be derived from ἀντὶ (anti) *against*, and *moine*, French for *monk*, from the fact that certain monks were poisoned by it.
Copper . . . (Cuprum)	Cu	From *Cyprus*, the name of the Mediterranean island where this metal was first worked.
Lead . . . . (Plumbum)	Pb	The Latin word is expressive of "something heavy," and the Saxon *læd* has a similar signification.
Mercury. . . (Hydrargyrum)	Hg	*Hydrargyrum*, from ὕδωρ (hudōr) *water*, and ἄργυρος (arguros) *silver*, in allusion to its liquid and lustrous characters. *Mercury*, after the messenger of the gods, on account of its susceptibility of motion. The old name *quicksilver* also indicates its ready mobility and argentine appearance.
Silver . . . (Argentum)	Ag	Ἄργυρος (arguros) *silver*, from ἀργὸς (argos) *white*. Words resembling the term *silver* occur in several languages, and indicate a white appearance.

The following are names of some of the less frequently occurring elements, compounds of which, however, are alluded to in the British Pharmacopœia, or are met with in pharmacy.

NAME.	SYMBOL.	DERIVATION OF NAME.
Bromine . .	Br	From βρῶμος (brōmos), a *stink*. It has an intolerable odour.
Fluorine . .	Fl	From *fluo*, to *flow*. Fluoride of calcium, its source, is commonly used as a flux in metallurgic operations.
Boron . . .	B	From *borak* or *baurak*, the Arabic name of *borax*, the substance from which the element was first obtained.
Silicon . . .	Si	From *silex*, Latin for *flint*, which is nearly all silica (an oxide of silicon).
Lithium . .	L	From λίθειος (litheios) *stony*, in allusion to its supposed existence in the mineral kingdom only.

NAME.	SYMBOL.	DERIVATION OF NAME.
Strontium . .	Sr	This name is commemorative of *Strontian*, a mining-village in Argyleshire, Scotland, in the neighbourhood of which the mineral known as *strontianite*, or carbonate of strontium, was first found.
Cerium . . .	Ce	Discovered in 1803, and named after the planet *Ceres*, which was discovered on Jan. 1, 1801. The oxalate of cerium is official, but seldom used.
Chromium . .	Cr	From χρῶμα (chrōma) *colour*, in allusion to the characteristic appearance of its salts.
Manganese . .	Mn	Probably the slightly altered word *magnesia*, with whose compounds those of manganese were confounded till 1740.
Cobalt . . .	Co	*Cobalus*, or *Kobold*, was the name of a demon supposed to inhabit the mines of Germany. The ores of cobalt were formerly troublesome to the German miners, and hence received the name their metallic radical now bears.
Nickel . . .	Ni	*Nickel*, from *nil*, *worthless*. Nickel ore was formerly called *Kupfernickel*, *false copper*. When a new element was found in the ore, the name nickel was retained for it.
Tin (Stannum)	Sn	Both words are possibly corruptions of the old British word *staen*, or the Saxon word *stan*, a stone. Tin was first discovered in Cornwall, and the ore (an oxide) is called *tinstone* to the present day.
Gold (Aurum) .	Au	*Aurum* (Latin) from a Hebrew word signifying the colour of fire. *Gold;* a similar word is expressive of *bright yellow* in several old languages.
Platinum . .	Pt	From *platina* (Spanish), diminutive of *plata*, *silver*. It somewhat resembles silver, but is less white and lustrous.
Bismuth . .	Bi	Slightly altered from the German *Wismuth*, derived from *Wiesematte*, "a beautiful meadow," a name given to it originally by the old miners in allusion to the prettily variegated tints presented by the freshly exposed surface of this crystalline metal.
Cadmium . .	Cd	*Καδμεια* (Kadmeia) was the ancient name of calamine (carbonate of zinc), with which carbonate of cadmium was long confounded, the two often occurring together.

Gold, Platinum, Tin, and Silicon are classed with the less important elements, because their salts are seldom used in pharmacy.

It will be noticed that the symbol of an element is simply the first letter of its Latin name, which is generally the same as in English. Where two names begin with the same letter, the less important has an additional letter added.

QUESTIONS AND EXERCISES.

Of how many elements is terrestrial matter composed?—In what state do the elements occur in nature?—Distinguish between the *art* and the *science* of chemistry.—What is the difference between an element and a compound?—Enumerate the chief non-metallic elements.—Describe a process for the preparation of oxygen.—How are gases usually stored? —Mention the chief properties of oxygen.—What is the source of animal warmth?—State the proportion of oxygen in air.—Is the proportion constant, and why?—Give a method for the elimination of hydrogen from water.—State the properties of hydrogen.—Why is a mixture of hydrogen and air explosive?—Explain the effects producible by the ignition of large quantities of coal-gas and air.—What is the nature of combustion?—Define a *combustible* and a *supporter of combustion*.—Describe the structure of flame.—State the principle of the Davy safety-lamp.—To what extent is hydrogen lighter than oxygen?—What do you mean by *diffusion* of gases?—State Graham's law concerning diffusion.—Name the source of phosphorus, and give its characters.—Why does phosphorus burn in air?—What remains when ignited phosphorus has removed all the oxygen from a confined portion of air?—Mention the properties of nitrogen.—What office is fulfilled by the nitrogen of the air?—State the proportions of the chief constituents of air.—Mention the minor or occasional constituents of air.—What is the proportion by weight of nitrogen to oxygen in the atmosphere?—Give the specific gravity of nitrogen.—How is chlorine prepared?—Enumerate the properties of chlorine.—Define the terms *deodorizer* and *disinfectant*.— Explain the bleaching effect of chlorine.—What proportion of hydrogen to chlorine is necessary for the formation of hydrochloric acid gas?—State the prominent chemical and physical characters of sulphur.—State those of carbon.—State those of iodine.—Give the derivations of the names of some of the elements.—What are the symbols of oxygen, hydrogen, nitrogen, carbon, chlorine, iodine, sulphur, phosphorus?

THE LEARNER IS RECOMMENDED TO READ THE FOLLOWING PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY CAREFULLY ONCE OR TWICE, THEN TO STUDY (EXPERIMENTALLY, IF POSSIBLE) THE SUCCEEDING PAGES, RETURNING TO AND READING OVER THE GENERAL PRINCIPLES FROM TIME TO TIME UNTIL THEY ARE THOROUGHLY COMPREHENDED.

THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

DEFINITION OF CHEMICAL ACTION.

The learner may now proceed to study the manner in which substances act chemically on each other. By acting *chemically* it will be obvious, from the preceding experiments, that what is meant is *so affecting each other that the substances are greatly altered in properties.* A *mixture* of free oxygen gas and hydrogen gas is still a gas; *a chemical compound* of oxygen and hydrogen is a liquid, namely, water; here is great alteration in properties. Iodine is only slightly soluble in water, and forms a brown coloured solution, and iron is insoluble; but when iodine and iron are *chemically* combined, the product is very soluble in water, forming a light-green solution in which the eye can detect neither iodine nor iron, and which is utterly unlike iron or iodine in any one of their properties. Sand, sugar, and butter, rubbed together, form *a mere mixture*, from which water would extract the sugar, and ether dissolve out the butter, leaving the sand. Tartaric acid, carbonate of sodium, and water, mixed together, form a *chemical compound* containing neither an acid nor a carbonate, these bodies having interacted and formed fresh combinations. These illustrations show that *chemical* action is distinguished from all other actions by (*a*) producing an entire change of properties in bodies. It also is (*b*) exerted only between definite weights and volumes of matter. This (*a* and *b*) cannot be said of any other action—the action of any of the other great forces of nature (gravitation, heat, light, electricity, etc.); hence the statements (*a* and *b*) furnish a sharp and precise definition of *chemical* action or the chemical force. Further (*c*) chemical action is only exerted when the substances are close together.

ATOMS.

In a chemical compound, what has become of its constituents? Let the reader place before him specimens of sulphur, iron, and sulphide of iron; or iodine, iron, solid iodide of iron, and its solution in water or syrup (*Syrupus Ferri*

Iodidi, B.P.). In the sulphide of iron, what has become of the sulphur and of the iron from which it was made? The *mixture* of sulphur and iron, in *combining* to form sulphide of iron, has not lost weight, and, indeed, by certain processes, it is possible to recover its sulphur as sulphur, and its iron as iron; so that we are compelled to believe (we cannot avoid the conclusion) that sulphide of iron contains particles of sulphur and of iron. But how small must be these particles! Rub a minute fragment to dust in a mortar and place a trace of the powder under the highest power of the best microscope; no yellow particle is visible, not the minutest portions of lustrous metal, but dull-brown miniature fragments of the original mass. The ultimate particles of sulphur and iron, or of the elements in any other compound (the chlorine and sodium in common salt, or the iodine and iron in solution of iodide of iron), are, in short, too small to be seen. Can they be imagined? Again, no! The mind cannot conceive of an ultimate particle (sulphur, iron, sulphide of iron, or what not) so small but what the next instant the imagination has divided it. Yet learner and teacher must have some common platform on which to reason and converse. The difficulty is met by speaking of these inconceivably small particles as *atoms* (ἄτομος, *atomos*, indivisible; from the privative *a* and τέμνω, *temno*, to cut—that which is not cut, or divided), an idea first thoroughly worked out by our countryman Dalton at the commencement of the present century.

The Greeks had a vague notion that matter could not be infinitely divisible; that there must be some limit to the divisibility of matter; that all matter must be made up of ultimate particles. Democritus, 400 B.C., held that matter was formed of atoms. But it was Dalton who, chiefly through employing the balance, gave exactitude to this notion, and, by his broad mental grasp, converted a vague hypothesis into a sound and satisfactory theory that all the world has since accepted and employed in explanation of the facts relating to those changes or alterations in matter which had up to his time proved so inexplicable. Doubtless the theory is only a theory. We may never be able to demonstrate the existence of atoms. But it is a theory supported by all known facts, one of those short reflections of facts dear to healthily constituted minds; moreover it is the only theory possible to the majority of minds in the present state of knowledge and education.

We cannot speak of iodine and iron uniting lump to lump, as two bricks are cemented together or blocks of wood glued together, for such is not the kind of action. We cannot select minute fragments of each to regard as the combining portions; for the minutest fragment we could obtain is visible, and iodide of iron contains neither visible iodine nor visible iron. And yet iodide of iron contains both iodine and iron, or, at least, a given weight of the compound is obtained from the same weight of constituents, and the same weight of constituents is obtainable from an equal weight of the compound. We might say that molecules are concerned in the operation; but a molecule means a little mass of—of what? there is positively no word left with which to carry on conversation and description but *atoms.* Any other mode of treating the matter is too subjective for general employment. Moreover, any difficulty in forming a definite conception of an atom is met by regarding an atom, not necessarily as something which *cannot* be divided, but as "a particle of matter which undergoes no further division *in chemical metamorphoses*" (*Kekulé*). Even physicists regard atoms from much the same point of view; indeed, they often speak of still larger portions of matter (molecules) as atoms, meaning thereby "something which is not divided *in certain cases that we are considering*" (*Clifford*). Dalton's Atomic Theory will again be referred to within the next twenty pages, more especially as explanatory of the curious fixedness of the weights and volumes in which elements and compounds alone combine with each other.

THE CHEMICAL FORCE.

What power binds the atoms of a chemical compound together in such marvellous closeness of union that in the couple or group they lose all individuality? Clearly an attractive force of enormous power, a force remotely resembling, perhaps, that which attracts a piece of iron to a magnet. Only by such an assumption can we conceive that common salt contains chlorine and a metal (sodium), or that wood contains carbon, hydrogen, and oxygen. Were not this force thus all-powerful, the carbon in wood would show its blackness and other qualities, and the hydrogen and oxygen give indications of their gaseous and other characters. This attractive force is commonly termed *the chemical force*, sometimes *chemical* *affinity.* The word *chemism* has also been proposed for it, just as the magnetic force is termed magnetism, but the word has not generally been adopted.

Whence comes the chemical force? Whence comes matter? We can neither create nor destroy matter; we can neither create nor destroy force. We can alter matter from one form to another; we can alter force from one form to another. The various forms of compounds are thus co-related; the various forces are co-related. But of the whence and whither, either of matter or of force, we know nothing.

MOLECULES.

A free, uncombined atom probably cannot exist in a state of isolation at common temperatures for any appreciable length of time. For we must regard an atom as the home of an attractive force of great intensity; and the moment such an atom is liberated from a state of combination (say, hydrogen from water, or chlorine from salt) it finds itself in proximity to another atom having similar desires for union, so to speak; the result is an impetuous rushing together and formation of either couples, trios, or groups, according to the nature of the atoms. It would be as difficult to conceive of separate atoms as to imagine that a strong magnet and a piece of steel could be suspended close to each other without being drawn together. It is, doubtless, possible to keep some pairs of atoms apart by the aid of heat, just as the magnet and steel may be parted by a superior amount of force; but such a condition of things is abnormal. These pairs and other groups of atoms are conveniently designated by the one word *molecule*, the diminutive of *mole*, a mass; literally, little masses. Dissimilar kinds of atoms seem to have greater attraction for each other than similar kinds; for, first, the masses of matter met with in nature in the great majority of cases contain two or more dissimilar elements; and, secondly, at the moment certain elements are liberated from their combinations, they are very specially active in combining with other, different, elements; that is to say, the chances are not equal that the liberated elements will either retain their elementary condition or combine to form compounds, but the cases in which compounds are formed are actually in great majority.

The study of the chemistry of molecules, *quâ* molecules, is of great interest; but the study of the chemistry of the atoms or groups of atoms within molecules is of enormously greater interest. A molecule of nitrogen, for instance, is not very active; an atom of nitrogen has activity which even the most advanced chemist finds difficult of realization.

RECAPITULATORY.

It is desirable that the learner should here make some experiment which will serve to bring again under notice in an applied or concrete form what has just been stated respecting the substances termed *chemical compounds*, and concerning the character of that *chemical force* which resides in the *atoms* of *molecules*. The following will usefully serve this purpose; it is the process for detecting a trace of sulphurous acid in common liquid hydrochloric acid.

As already proved, hydrogen gas and chlorine gas, when inter-united in a manner presently explained, form hydrochloric acid gas: the latter dissolved in water is the ordinary colourless liquid of the shops termed *Hydrochloric Acid*, the *Acidum Hydrochloricum* of pharmacopœias. Common, yellow, acid not infrequently contains as an impurity a trace of sulphurous acid gas, a body also already mentioned and experimentally prepared—a trace too small to be detected by its odour. Obtain a specimen of common liquid hydrochloric acid containing as an impurity a trace of sulphurous acid, or adopt the more simple course of purposely adding a few drops of aqueous solution of sulphurous acid (*Acidum Sulphurosum*,* B.P.) to some hydrochloric acid. (If no sulphurous acid is at hand, the object may be accomplished by putting a quarter or half an ounce of liquid hydrochloric acid into a wide-mouthed bottle, then burning a fragment of sulphur on a wire or strip of wood inside the bottle for a few seconds, and shaking the gas and liquid together.) Pour some of the impure liquid hydrochloric acid into a test-tube, add about an equal bulk of water, and then drop in a few fragments of the metal zinc. Effervescence will occur, due to the escape of inodorous hydrogen gas, together with a small quantity of a badly-smelling gas termed sulphuretted hydrogen. Bring the mouth of the tube near the nose; the presence of sulphuretted hydrogen will at once be recognised.

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* These aqueous solutions of acids are generally, for the sake of brevity, simply termed acids.

The hydrochloric acid has now been *tested* for sulphurous acid. If the experiment be performed on any commercial specimen of the acid, and a smell of sulphuretted hydrogen be observed, the operator will at once be able to state that the specimen contains sulphurous acid as an impurity.

Now, using Dalton's theory of the atomic constitution of matter, the explanation of what occurs in the successive steps of the foregoing experiment is as follows:—

Hydrochloric acid is a *chemical compound* of hydrogen and chlorine. That it is a chemical compound, and not a mere mechanical mixture of hydrogen and chlorine, is shown by the fact that its properties are altogether different from the properties of its constituents. The attractive power or *chemical force* resident in the *atoms* of the *molecules* of chlorine and of hydrogen has caused the atoms to combine in the closest manner imaginable and form pairs of atoms or *molecules* of the chemical compound—hydrochloric acid. Zinc being introduced into the acid, and the atoms of zinc and chlorine having even still greater attraction for each other than the hydrogen for the chlorine, the zinc and chlorine atoms combine and form a new molecule (termed chloride of zinc) which remains in the liquid, while the hydrogen atoms, having the atoms of no other element to combine with if the acid is pure, unite to form pairs, or molecules, of hydrogen, and in that state escape from the vessel. If the acid be impure from the presence of sulphurous acid (sulphurous acid gas, it will be remembered, is a compound of sulphur and oxygen), some of the hydrogen atoms, at the moment of birth, their *nascent* state (from *nascor*, to be born)—the specially active state—finding the atoms of other elements present, namely, the atoms of sulphur and oxygen of the sulphurous acid molecules, combine by preference with these atoms and form new molecules, the sulphur and hydrogen forming sulphuretted hydrogen, and the oxygen and hydrogen producing water—the former escapes with the great bulk of the hydrogen, while the water remains with the water already in the vessel.

Note.—Ordinary hydrogen gas—that is, hydrogen in the molecular, not in the atomic or nascent condition—will not thus attack sulphurous acid. Doubtless the amount, or extent of attraction of two atoms of hydrogen for one atom of, say, the sulphur in the sulphurous acid molecule, is a constant amount; but the uncombined, nascent atoms can, it is only fair to suppose, get much nearer to the attacked molecule than they can after they have themselves combined to form a molecule, molecules (but scarcely atoms) having an appreciable amount of space between them, as will be further shown almost immediately. In other words, it is probably distance which prevents an attack which would be inevitable at close quarters. These remarks apply to all similar reactions of other elements. The great activity of nitrogen in what the student will now see is its atomic rather than merely nascent condition, as compared with its slight activity in what now may be termed its molecular condition, has already been alluded to (page 18).

Conditions and Nature of the Manifestation of the Chemical Force.

The exertion of chemical affinity is only possible when the masses of the bodies touch. Thus it was necessary to bring the oxygen, hydrogen, phosphorus, chlorine, sulphur, carbon, iodine, and iron into ordinary contact, in the respective experiments with those elements, before the various reactions occurred. The exact nature of these actions, as indeed of all in which substances act chemically, would seem to be an interchange, most generally a mutual one, of the atoms of which the molecules consist—a change of partners, so to speak. Thus, in the experiment in which hydrogen and chlorine gases united to form hydrochloric acid gas, a pair of atoms in a hydrogen molecule and a pair of atoms in a chlorine molecule, finding themselves opposite to each other, changed places, the atoms of each of the old molecules unlinking, so to say, and pairing off in fresh couples.

$$\left\{\begin{matrix}\text{Hydrogen}\\ \text{Hydrogen}\end{matrix}\right\}\text{and}\left\{\begin{matrix}\text{Chlorine}\\ \text{Chlorine}\end{matrix}\right\}\text{become}\left\{\begin{matrix}\text{Hydrogen}\\ \text{Chlorine}\end{matrix}\right\}\text{and}\left\{\begin{matrix}\text{Hydrogen}\\ \text{Chlorine}\end{matrix}\right\}$$

Or, using the symbols of these elements instead of the full names, $H\,H$ and $Cl\,Cl$ become $H\,Cl$ and $H\,Cl$. Still further economizing space and trouble, the statement may be made in the following form:—H_2 and Cl_2 become 2HCl. Once more, by using the *plus* sign (+), instead of the words "and" or "added to," and the sign or symbol = or *equal*, instead of the words "become" or "are equal to," we reach the shortest expression:—$H_2 + Cl_2 = 2\,H\,Cl$, and this is the form in which it may be expressed in the student's note-book. It is the shortest and most convenient form, and is instructive and suggestive to the mind.

Chemical Notation.

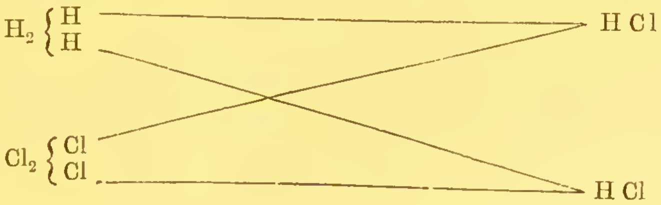
We have thus gradually arrived at a spot in the path of chemical philosophy at which we must halt to more fully discuss the usual method of recording chemical travels. We have arrived at the subject of *chemical notation* (from *noto*, to mark), the art or practice of recording chemical facts by short marks, letters, numbers, or other signs. Already the first capital letter, or the first and one of the following small letters of the Latin names of the elements have been employed as contractions, or shorthand expressions, or *symbols* of the whole *name*. Thus H has been used for the word "hydrogen," and Cl for "chlorine." A *second function* of such a symbol is that of indicating one *atom*. Thus H stands not only for the word or substance "hydrogen," but for one atom of hydrogen. Large and small figures (2 or $_2$) indicate a corresponding number of atoms, the small figure only multiplying the one particular symbol to which it is attached, while a large figure multiplies all the symbols it precedes. Thus H_2 means two atoms of hydrogen, and Cl_2 two atoms of chlorine; while 2HCl means two atoms of hydrogen and two atoms of chlorine, or, in one word, two molecules of hydrochloric acid gas. A *third function* of such a symbol as H or Cl is that of indicating one *volume* of the element in the gaseous state. Thus H, Cl, or O, stand, first, for the substances named hydrogen, chlorine, and oxygen; secondly, for single atoms of hydrogen, chlorine, and oxygen; thirdly, they represent single and equal volumes of chlorine, hydrogen, and oxygen. It will be remembered that one test-tubeful of hydrogen and an equal-sized test-tubeful of chlorine were employed, in a previous experiment, in forming hydrochloric acid gas, HCl.

The *position* of symbols counts for something. Thus, HCl indicates not only the substances hydrogen and chlorine, single atoms of each of the substances, and equal volumes of each, but also that the two substances are *joined together by the chemical force.* If the two letters were placed one under the other, or at some distance apart, or were separated by a comma or a plus sign (+), they would be understood to mean a mere *mixture* of the elements ; but placed as close as the printer's types will conveniently and consistently allow, they must be considered to stand for a *compound* of the elements, that is to say, hydrochloric acid gas (HCl). The collection of symbols representing a molecule is termed a *formula.* H_2, Cl_2, and HCl are the *formulæ* of hydrogen, chlorine, and hydrochloric acid gas.

$$H_2 + Cl_2 = 2HCl.$$

Such a set of letters, figures, and marks as that on the above line is collectively termed an *equation*, because it indicates the equality of the number and nature of the atoms before and after chemical action. On the left-hand of the sign of equality (=) are shown two molecules, and on the right-hand two molecules; but of the molecules on the left, one contains two atoms of hydrogen and the other two atoms of chlorine, while of the molecules on the right each contains one atom of hydrogen and one of chlorine. The equation forms a short and convenient plan of recording the facts of experiment.

Instead of an equation, a *diagram* may be employed to exhibit the same facts. Thus :—



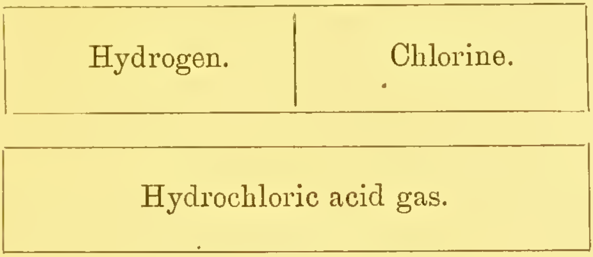
PHYSICAL AND CHEMICAL CONSTITUTION OF MATTER.

RELATIONS OF GASES, LIQUIDS, AND SOLIDS.

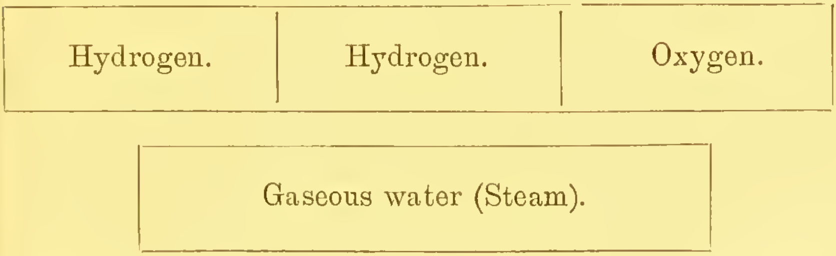
Molecules of gases are not in absolute contact, for a volume of gas may be compressed with very little force to half or one-fourth its bulk—in short, to such an extent that in many cases the molecules sufficiently approximate to form a liquid

In a liquid the molecules are still free to glide about with ease amongst each other; and though in solids they exhibit less mobility, still even solids may be compressed by powerful pressure, so that probably in *no* instance are molecules in absolute contact. (Moreover, from the researches of Caignard de la Tour, and of Andrews, there would seem to be no sharp lines of demarcation between the gaseous, liquid, and solid conditions of substances.) One's mental picture of the relative position of the molecules of gaseous, vaporous, liquid, or solid matter must be such a picture as that of the moving particles of dust in the air of a room, or such a relation to each other as that of the planets and stars suspended in space. There is abundant experimental evidence to warrant such a conception. A clear, transparent fluid appears perfectly homogeneous, but is not so. Its particles are not in contact. Every person who has mixed 5 pints of rectified spirit with 3 pints of water knows that the 100 fluid ounces of spirit and 60 fluid ounces of water do not when mixed give 160 ounces of "proof" spirit, but only 156 ounces; the molecules of the liquids have gone closer together, having probably a little attraction for each other. Having gone closer together, they were not previously so close together; the necessary conclusion being that even liquids are porous. Why a gas under pressure should immediately return to its original bulk when the pressure is removed, while a liquefied or solidified gas only slowly resumes the gaseous or vaporous state, is a question which requires for discussion a knowledge of the nature of forces other than the chemical. For it must be remembered that the study of the chemical force is mainly the study of the internal constitution of molecules; the study of the properties of entire molecules forming the domain of Physics, sometimes termed Natural Philosophy. (Physics, from φύσις, *phusis*, nature; that is, visible and material Nature; the study of actions and reactions which do not involve entire and permanent change in the properties of bodies—the study of the action of heat, light, electricity, magnetism, gravitation, etc., on matter.)

It is necessary, however, to state something more about the physical as well as the chemical condition of the molecules of a *gas*, in order that the learner may be prepared for the fact that mixtures of certain gaseous elements, in combining to form gaseous compounds, diminish considerably in volume. Thus, while a pint of hydrogen and a pint of chlorine give a quart of hydrochloric acid gas,—



two pints of hydrogen and one of oxygen are necessary to produce a quart of gaseous water (steam). It will be remembered that two volumes of hydrogen and one of oxygen were necessary in a previous experiment in which water was formed.



Now, that a pint of hydrogen gas and a pint of chlorine gas should, after chemical reaction or rearrangement of the atoms of the molecules has taken place, form two pints of hydrochloric acid gas, is quite what we should expect. For, first, the reader, by this time, is not astonished that chemical combination is attended by entire change of properties; and, secondly, the experience of years has led him to expect that a pint of one thing added to a pint of another gives two pints of the mixture. But that two pints of hydrogen and one pint of oxygen should, after combination (and under like conditions of temperature and pressure), give, not three, but two pints of product (steam) is perhaps somewhat astonishing and needs explanation. To this end let us *picture* a few of the molecules of hydrogen and as many molecules of chlorine. Draw with a pencil on paper several pairs of crosses (+ +) to represent hydrogen molecules, and circles (○ ○) for chlorine molecules, or, if coloured ink is at hand, red pairs of dots for hydrogen and green for chlorine. Or, at once, for facility in printing, let the following pairs of letters *h h* represent a few (say, nine) molecules of hydrogen, and *c c* molecules (nine) of chlorine—before combination :—

h h	*h h*	*h h*	c c	c c	c c
h h	*h h*	*h h*	c c	c c	c c
h h	*h h*	*h h*	c c	c c	c c

Then, after combination, we shall have eighteen molecules of hydrochloric acid gas :—

h c	*h* c	*h* c	*h* c	*h* c	*h* c
h c	*h* c	*h* c	*h* c	*h* c	*h* c
h c	*h* c	*h* c	*h* c	*h* c	*h* c

But when two volumes of hydrogen and one of oxygen combine and give two volumes of steam, the mental picture must be, not that of molecules somewhat nearer to each other than before, nor any difference in the size of the molecules, but a picture of molecules each containing three instead of two atoms—thus, still using pairs of letters, just for the moment, to represent a few (the space will allow only twenty-seven) molecules:—

h h	*h h*	*h h*	*h h*	*h h*	*h h*	o o	o o	o o
h h	*h h*	*h h*	*h h*	*h h*	*h h*	o o	o o	o o
h h	*h h*	*h h*	*h h*	*h h*	*h h*	o o	o o	o o

The twenty-seven molecules (eighteen hydrogen, nine oxygen) will, after combination, become eighteen molecules of steam :—

hoh	*hoh*	*hoh*	*hoh*	*hoh*	*hoh*
hoh	*hoh*	*hoh*	*hoh*	*hoh*	*hoh*
hoh	*hoh*	*hoh*	*hoh*	*hoh*	*hoh*

As already suggested, one's mental picture of a number of molecules may well give them such a relation to each other as that of a number of solar systems in the universe, equally distant from each other, and each occupying a similar space, yet one system containing a sun and one planet, another a sun and two planets, and so on, or even one or more of the planets having one or more moons. Indeed, the atoms in some very complex molecules really appear to have very much the relation to each other of the sun, planets, and moons of a solar system. To indicate such molecules by letters as above would of course require more space than is there given to the assumed pictures of molecules.

Here occurs an opportunity that must not be lost of stating a mode of reasoning by which a molecule of oxygen (or of many other elements) is shown to be a double structure—shown to contain two atoms. Five equal-sized bottles are before us, two filled with hydrogen, one with oxygen, and two with steam. (The bottles are hot enough to prevent the steam condensing to water, and all five are at the same temperature.) Apply heat so that all shall be equally heated, *the three different substances expand equally.* Cool equally, *the contents contract equally.* Apply equal pressure to all five, *each is equally affected.* Diminish pressure equally, *each portion of the three substances equally expands.* Gases (practically steam is a gas, it is simply not a permanent gas) —gases thus similarly affected must be, *physically*, similarly constructed or constituted (a law which will again be referred to on page 52); each bottle must contain the same number of particles or molecules, and at any one temperature and pressure the molecules in each must be equally distant from each other. We do not know what actual number or distance, but whatever be the number and distance, it is the same for each bottle. Say that one million is the number, then we shall have a million of molecules in the first hydrogen bottle, a million in the second, a million in the oxygen bottle, and a million in each of the steam bottles. We will cause chemical combination between the two millions of hydrogen molecules and one million of oxygen molecules, producing (as we have seen) two millions of steam molecules, having the properties already stated. But a molecule of steam contains an atom of oxygen. Hence two millions of steam molecules contain two millions of oxygen atoms, which two millions of oxygen atoms have been obtained from one million of oxygen molecules. Therefore each molecule of oxygen was a double structure—

each molecule of oxygen contained at least two atoms of oxygen. As Clifford says, "you cannot put 50 horses into 100 stables, so that there shall be exactly the same amount of horse in each stable; but you can divide 50 *pairs* of horses among 100 stables."

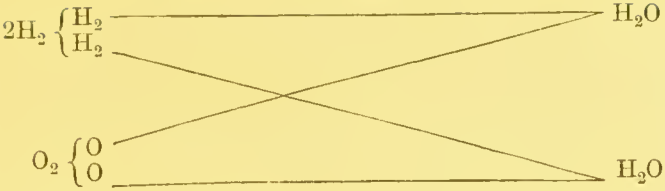
Thus much respecting the construction of gaseous or vaporous matter. Our knowledge of the constitution of liquid and solid matter is still more limited.

With regard to the notation of the subject, it will be sufficient to state here, that while a *symbol* usefully represents one volume of any gas, *a formula of any gas or vapour represents two volumes.* By remembering this general rule we may, by looking at a formula, tell how many volumes of constituents were concerned in the formation of a compound, and therefore what amount of condensation, if any, occurred during the act of formation. By thus reading and interpreting the formula for water, H_2O, we see that two volumes of steam (at any temperature) may be obtained from two volumes of hydrogen and one volume of oxygen (at the same temperature), and thus that the extent of condensation when hydrogen and oxygen (at a stated temperature) unite to form gaseous water (at the same temperature) is from three to two. This subject will again be treated of in connection with Chemical Combination and the Specific Gravity of Gases.

Further Remarks on General Chemical Notation.

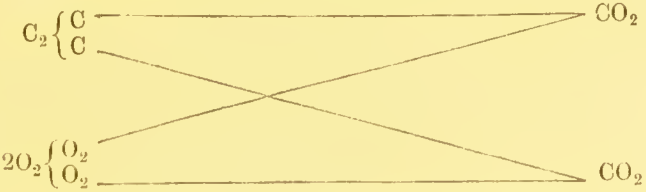
We may now take an experiment already made as an additional example of chemical action, and describe the simplest way of expressing the same by notation. When two volumes of hydrogen and one of oxygen were caused to combine, the production of flame and noise proved that chemical action of some kind had taken place; had the experiment been performed in dry vessels, evidence of the precise action would have been found in the bedewing produced by the condensation of the water on the sides of the tube. Similar evidence was afforded on holding a cool glass surface over the hydrogen-flame. The action is expressed in the following equation:—$2H_2 + O_2 = 2H_2O$.

Instead of this equation, the following diagram may be employed:—


$2H_2 \begin{cases} H_2 \\ H_2 \end{cases}$
$O_2 \begin{cases} O \\ O \end{cases}$
H_2O
H_2O

The foregoing aggregation of symbols or shorthand characters, or *formula*, H_2O, is, then, a convenient picture of the facts that have already come before us, viz., that water is formed of the elements hydrogen, H, and oxygen, O ; moreover, that it is formed of two measures or volumes of hydrogen, H_2, to one of oxygen, O ; and, thirdly, that the molecule of water (H_2O) is formed of two atoms of hydrogen (H_2) and one of oxygen (O). The formula also fulfils the *fourth function* of indicating that the two volumes of hydrogen and one of oxygen in combining condensed to two volumes of steam. That the resulting bulk of steam afterwards shrunk most considerably in condensing to water, is another matter altogether, a physical and not a chemical result, and due to the approximation of the molecules of water *after* formation.

Another experiment already performed, illustrating the character of the manifestations of chemical force (symbolically noted as follows), was that in which the red-hot carbon of wood was plunged into oxygen. The evidence of chemical action in that case was the sudden inflammation of the carbonaceous extremity of the wood. The particles of carbon and oxygen having intense attraction or affinity for each other at that temperature, rushed together so impetuously as suddenly to produce a large additional quantity of heat, an amount sufficient to cause the particles to emit an intense white light. The action is expressed on paper in either of the following ways :—$C_2 + 2O_2 = 2CO_2$; or,


$C_2 \begin{cases} C \\ C \end{cases}$
$2O_2 \begin{cases} O_2 \\ O_2 \end{cases}$
CO_2
CO_2

CO_2 is the formula of the well-known gaseous body commonly termed carbonic acid gas

The reader should here draw for himself equations or diagrams similar to those on pages 37 and 43, and thus show the formation of the three other bodies he has already produced—namely, phosphoric anhydride (P_2O_5), sulphurous acid gas (SO_2), and iodide of iron ($Fe\ I_2$), submitting the same, if possible, to a tutor or other authority to assure himself of their correctness.

Note.—In the foregoing experiments several illustrations occur of the formation of compounds having the gaseous, liquid, and solid conditions, in one of which three forms all matter in the universe apparently exists.

LAWS OF CHEMICAL COMBINATION (BY WEIGHT).

Chemistry as a *science* is little more than a hundred years old, though very many of the facts and operations we now term chemical have been known as isolated items of knowledge for centuries. Thus the ancient Egyptians made glass, vitriol, soap, and vinegar; and the Greeks started the idea that matter was composed of a few elements, imagining earth, air, fire, and water to be elements. In short, chemistry as an *art* was already very extensive a hundred or more years ago. But the great general principles which interlace and bind together separate facts, those which from their extensive application and importance are denominated *laws*, have all been brought to light since the year 1770. Scarcely more than a single century ago, Lavoisier, by invoking the aid of the balance, converted the *art* into the beginning of a *science* which has since grown by ever-recurring leaps and bounds. (Lavoisier was born in 1743, he was guillotined by Robespierre in 1794. A request for a few days of respite to complete some researches was refused on the ground that "the republic has no need of chemists.")

First Law relating to Chemical Combination.

Between 1785 and 1800, Bryan Higgins, William Higgins, Wenzel, Richter, and Proust, made analyses and researches which led up to the following generalization:—*When compounds unite to form definite chemical substances, they always combine in the same proportions.* The curious character of this fact could but be most striking, and indeed is so now, to the mind receiving it for the first time. Thus water (a compound) added to quicklime (a compound) gives slaked lime, a perfectly definite chemical substance. But whereas sand and water, sugar and water, sand and sugar, and such *mechanical* mixtures may be obtained by adding together the ingredients in any proportions whatever, say, 90 of sugar and 10 of sand, or 10 of sugar and 90 of sand, such a *chemical* mixture as slaked lime (say 100 parts) invariably results from the combination of $75\frac{3}{4}$ of quicklime and $24\frac{1}{4}$ of water. If a larger proportion than $75\frac{3}{4}$ per cent. of quicklime be employed, the excess remains as quicklime mixed with the slaked lime; and if more than $24\frac{1}{4}$ per cent. of water be used, an excess of water remains with the slaked lime and evaporates if the mixture be exposed to the air. Dalton discovered that when *elements* unite to form a definite substance, they, like compounds, always combine in the same proportions; and he was the first to set forth the law in a manner which was at once clear and comprehensive enough to include the former generalization. Thus:—

A definite compound always contains the same elements in the same proportions.

Take another example. Common salt always contains $39\frac{1}{3}$ per cent. of the metal sodium to $60\frac{2}{3}$ of chlorine, and water always 89 of oxygen to 11 per cent. of hydrogen (more exactly 88·89 to 11·11). As with the quicklime and water, so with the chlorine and sodium, and the constituents of many (not *all*) chemical compounds; in such cases, if either be added to the other in any quantity beyond stated proportions, the excess plays no part whatever in the act of combination. (In *some* cases, as will be seen directly, excess of either plays a very simple but very remarkable part.) In short, whether a compound be made directly from its elements, or by the combination of other compounds, or indirectly as one of two products of the action of substances chemically on each other, whatever be its origin, if it is a definite compound, it *always contains the same elements in the same proportions.* This is the first of the two laws governing chemical combinations.

Second Law relating to Chemical Combination.

Dalton further made such experimental researches as enabled him to lay down a second great law. He found that while many substances only united chemically in one proportion, others combined in two or even more; and he studied several such naturally related bodies. He found that while carbonic oxide (a gas formed when charcoal is burned with a limited supply of air) contains such a proportionate weight of carbon and oxygen as is represented by (to use the simplest figures) 3 and 4, carbonic acid (a gas formed when charcoal is burned with excess of air) contains 3 of carbon to exactly twice 4 of oxygen. He proved that a similar relation existed between two compounds of carbon and hydrogen, and between a cluster of compounds of nitrogen and oxygen. The first of the latter, to a given quantity of nitrogen, contains a certain proportion of oxygen; the next, to the same quantity of nitrogen, has exactly twice the proportion of oxygen; and the others have exactly three, four, and five times as much oxygen as the first, the quantity of nitrogen remaining the same throughout. Dalton thus generalized these facts :—

When two elements unite in more than one proportion, the resulting compounds contain, to a constant proportion of one element, simple multiple proportions of the other—or the weights of the constituent elements bear some similar simple relation to each other.

Thus carbonic oxide gas is a definite compound always containing fixed proportions of carbon and oxygen, and carbonic acid gas is also a definite compound always containing fixed proportions of carbon and oxygen. Both thus obey the first law of combination. But whereas carbonic oxide contains, or may be made from, 30 parts (ounces, grains, or other weights) of carbon and 40 of oxygen, carbonic acid contains, or may be made from, 30 parts of carbon and exactly twice 40 of oxygen.

The second law cannot but be as striking as the first when freshly unveiled to the mind. Sand and sugar, or any substances which do not act *chemically* on each other, may be mixed in the proportions of 30 to 40, 30 to 80, 30 to 60, or any other quantities; but if an attempt be made to burn 30 parts of carbon in 60 of oxygen, the elements will themselves naturally assert their own special combining powers, and refuse, so to say, to unite in these proportions: the 30 of carbon will first combine with 40 of oxygen and form

70 of carbonic oxide; and this gas, which, had it the opportunity, would combine with 40 more of oxygen and form carbonic acid gas, finding only half that quantity, namely 20 of oxygen, present, contents itself by one half (that is 35 of carbonic oxide) accepting the 20 of oxygen and becoming carbonic acid gas, while the other half remains as carbonic oxide. This is a most wonderful fact. Again, if 30 parts of carbon be burnt in more than 80, say 85, of oxygen, only 80 will be used, the other 5 remaining as oxygen merely *mixed* with the resulting carbonic acid gas. If we attempt to burn 30 parts of carbon in less than 40 of oxygen, the oxygen will take up three-fourths its weight of carbon and form carbonic oxide, while the excess of carbon will remain as carbon.

RECAPITULATION.

Nature does not always permit man to mix things in any proportions he pleases. She does sometimes. She does if he only stirs things together, or if he only uses the attractions of adhesion or cohesion in binding the materials together; but if he employs chemical attraction, she restricts him to special proportions. That is to say, if the things mixed do not attack one another or intimately combine, then admixture may be effected in any proportion; and the mixture is a mere mixture having the mean properties of its components. Examples of such mixtures are seen in compound plasters, pill-masses, confections, and plum-puddings. But if the things do unite to form, not a mere mixture having the mean properties of its components, but a compound having new and distinct and definite characters of its own, then Nature does not permit man to combine the things in any proportion he pleases. The proportion is a fixed and constant one; and if he substitutes proportions of his own, the things unite in the proportions fixed by Nature, and the excess he has added either remains in its original uncombined condition, or it combines with the compound already produced to form a second *different* compound. Any one compound, that is, the *same* compound, always contains the same elements in the same proportions, and can only be made from the same elements in the same proportions. An attempt to mix the same elements in other proportions would result in one of two failures, namely, either the extra proportion would remain free and uncombined, or it would combine and convert the first compound, or a portion of it, into a *different* compound. The fresh compound thus produced, like the first, and indeed like all definite compounds, of course always contains the same elements in the same proportions.

In short (law 1), any definite compound always contains the same elements in the same proportions, and (law 2) any two elements uniting in more than one proportion unite in multiples of that proportion, and produce so many different definite compounds. Taking hydrogen as uniting in proportions of 1, oxygen unites in proportions of 16—that is 16, twice 16, thrice 16, and so on, never in intermediate proportions. Carbon unites in 'proportions of 12, sulphur of 32, chlorine $35\frac{1}{2}$. Every element (see the Table in front of the Index) has its combining proportion fixed by Nature.

The student of chemistry is recommended to accept these two great natural facts, great enough to be dignified by the name of *laws*, in all their inherent solidity and simplicity. Of course he will wonder *why* substances should combine, chemically, only in fixed proportions when forming a definite body, and *why*, when a substance combines in more than one proportion to form different definite bodies, the proportions should only be multiple proportions; and will gladly hail the extremely ingenious and useful explanation of these truths suggested by Dalton (*see* foregoing and following paragraphs on the theory that matter is built up of atoms). But man has not yet succeeded in so questioning Nature as to gain from her a *satisfactory* answer to such questions; and until he does succeed, any hypothesis, even Dalton's, should be held intelligently, but not too tightly. The facts themselves, however, should be grasped with the student's utmost tenacity.

Reciprocal proportions.—Careful consideration of the foregoing two great laws relating to chemical combination, leads to an important truth, namely:—*The proportions in which two elements unite with a third are the proportions (or simple multiples or submultiples of the proportions) in which they unite with each other.* Thus oxygen in proportions of 16 unites with hydrogen, and carbon in proportions of 12 unites with hydrogen; therefore 16 and 12 are the proportions in which oxygen and carbon will unite with each other.*

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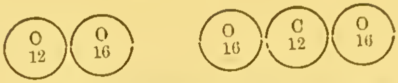
* See Axiom 1 in Hawtrey's "Introduction to the Elements of Euclid," Longmans & Co., 2*s*. 6*d*., a book recommended to any student who is not familiar with the mode of reasoning termed geometrical.

The Atomic Theory.

The laws which Dalton so largely aided to unveil—two grand and wonderful truths—he explained and correlated by a simple and beautiful hypothesis (1803 to 1808). *Why* should any given compound always contain the same elements in such absolutely *fixed* proportions? *Why*, when an element combines in more than one proportion, forming more than one given compound, should it combine in exactly *multiple* proportions? The first answer must be that no one knows—that is to say, that we are unable to refer to any demonstrable *fact* for the answer. But a century ago the same Englishman devised an *explanation* that has satisfied the world. Dalton's explanation was *that matter was not infinitely divisible, but composed of minute particles or* ATOMS *having an invariable character.* In the words of Wurtz, "*To an old and vague notion he attached an exact meaning, by supposing that the atoms of each kind of matter possess a constant weight, and that combination between two kinds of matter takes place not by penetration of their substance, but by juxtaposition of their atoms.*" Dalton raised the old Grecian hypothesis (see page 30) to the dignity and importance of theory, and gave to it a quantitative foundation.

Under this "atomic theory," carbonic oxide is a definite compound always containing the same elements in the same proportions, *because* each particle of it is composed of an atom of carbon and an atom of oxygen chemically united, the weights of the atoms being in the proportion of 3 and 4; that is, having a constant weight of 12 and 16, as we now believe. Carbonic acid gas is also a definite compound always containing the same elements in the same proportions, and the proportion of oxygen is just double that in carbonic oxide, *because* each particle of it is composed of an atom of carbon (weighing 12), and two atoms of oxygen (each weighing 16).

The healthily constituted student-mind asks, "*Why* an element should unite in exactly multiple proportions if it forms several compounds?" Because those compounds are "made" of atoms which, being indivisible, must, if they unite at all, unite 1 to 1, 2 to 1, 3 to 1, and so on. With such an explanation, although only one explanation, the healthily constituted mind gains desired satisfaction.



IMAGINARY PICTURES OF MOLECULES OF CARBONIC-OXIDE GAS AND CARBONIC ACID GAS.*

Again, the facts that with 12 of carbon oxygen unites in the proportion of 16, or a multiple of 16; that with 12 of carbon sulphur unites in the proportion of 32, or a multiple of 32 (the liquid known as disulphide of carbon is a chemical compound of 12 of carbon to twice 32 of sulphur); and thirdly, that oxygen and sulphur unite in proportions of 16 and 32, are at once explained on the assumption that these elements exist in atoms which have the respective weights mentioned. Existing in indivisible particles (atoms), which weigh 16, 12, and 32, oxygen, carbon, and sulphur *must* unite in indivisible weights of 16, 12, and 32.

Atomic Weights.

What has just been stated respecting two or three elements, is true of all the elements. It is a fact that when elements unite with one another in the peculiar and intimate manner termed chemical, they do not combine in the haphazard proportions of a mere mixture, but in one fixed and constant proportion. Such proportions or weights represent, according to Dalton, the weights of their atoms. Oxygen unites with other elements in proportions of 16, therefore 16 is the weight of the atom of oxygen. Chlorine unites with other elements in proportions of $35\frac{1}{2}$, therefore $35\frac{1}{2}$ is the atomic weight of chlorine. And for a similar reason the atomic weight of hydrogen will be 1, carbon 12, sulphur 32, nitrogen 14, and iodine 127. Of course it will be understood that these are the *relative* weights of atoms, for we cannot know the absolute weights. All that is known is that the chlorine atom, for instance, is 35·5 times as heavy as the hydrogen atom, whatever the absolute weight of the latter may be, and the iodine atom 127 times as heavy. The quantity of metal which with 35·5 of chlorine will form a chloride, and with twice 35·5 a second chloride (dichloride of bichloride), will require 127 of iodine to form an iodide; and twice 127 of iodine to form a second iodide (a diniodide or biniodide).* In other words, the atomic weight of an element is the *ratio* of the weight, quantity of matter, or mass of an atom, to the weight, quantity of matter, or mass, of an atom of hydrogen.

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* The size of atoms, their shape, their absolute weight—whether or not they are in actual contact—whether or not they are fixed in relation to each other, free to move about each other, or in a constant state of motion—and whether or not the chemical force actuates them as the force of gravitation influences our earth and moon and solar systems, are matters of which at present we know almost nothing. The two pictures are not intended to convey any impression that the following formulæ do not give:—CO or OC, OCO or CO_2.

Notes on Notation.—A *fourth function* of a symbol is to represent atomic *weight.* Thus the symbols H, Cl, O, etc., not only perform the offices of representing (*a*) names, (*b*) single volumes, and (*c*) single atoms, but (*d*) definite weights of the respective elements. H=1, Cl=35·5, O=16, I=127, N=14, K=39, etc.

Laws of Chemical Combination (by Volume).

In 1809 Gay-Lussac showed it to be a fact that when gaseous elements unite with one another in the intimate manner termed chemical, they do not combine in the haphazard proportions (that is, proportions by measure or volume) of a mere mixture, but in constant proportions in the case of any single definite compound, and in simple multiple proportions in cases where two elements form more than one definite compound. He thus proved that the laws respecting the constancy of weight with which elements combine hold good with reference to volume, at all events in those cases in which elements exist in or can be made to assume the gaseous condition. A volume of hydrogen gas and an equal one of chlorine gas give hydrochloric acid gas. Two volumes of hydrogen and one of oxygen give water-vapour or steam. Such volumes or simple multiples are alone the proportions by bulk in which elements combine. If any excess of either gas be mixed and combination attempted, only the stated proportions really combine, the excess remaining unaltered. Further, following Gay-Lussac, on weighing these similar and equal volumes of hydrogen, chlorine, and oxygen, we find that the chlorine is 35·5 times as heavy as hydrogen, and oxygen 16 times as heavy as hydrogen.

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* Only the atomic weights of the above and a few of the chief metallic elements need be committed to memory; others can be sought out as occasion may require. A Table of *combining proportions* of elements, or atomic weights, is given at the end of the volume—in front of the Index.

Avogadro's "Law."—Avogadro in 1811, and Ampère in 1814, reasoning on the fact that all gases are similarly affected by variations of pressure (Boyle, 1662, verified by Mariotte) and temperature (Charles), (see also p. 40), concluded that all gases must be similarly constituted (similarity in properties always indicating similarity in character or nature, a mode of reasoning, or deducing, or inferring, that even children soon naturally adopt in dealing with everything that appeals to their senses); in other words, that if *equal volumes of gases* be taken *under like conditions*, each will *contain the same number of molecules*, similar in size and equally distant apart. The deduction is obvious. *The weights of molecules of gaseous elements (that is, of pairs of atoms, and therefore of atoms themselves) must differ to the extent that the weights of equal volumes of those elements differ.* Equal volumes of hydrogen, chlorine, and oxygen, weighing respectively 1, 35·5, and 16, and each of these volumes containing an equal number of molecules, each formed of two atoms, it follows that the relative weights of the atoms will be 1, 35·5 and 16.

It will thus be seen that the weight of the *volume* in which an element combines, and the *actual weight* in which it combines, irrespective of volume, are identical. For instance, we should find by experiment that, as a simple matter of fact, oxygen unites with other elements in proportions of 16 by weight, while hydrogen combines in proportions of 1. Turning, then, to experiments on the volumes in which hydrogen or oxygen combine, and having ascertained those volumes, and then having weighed them, we should find that the oxygon volume weighs 16, while the hydrogen weighs 1. In compounds in which proportions of 1 grain of hydrogen were found, oxygen would be found in proportions of 16 grains. In gaseous compounds in which hydrogen existed in proportions of, say, 27 ounces by measure, oxygen would bo found in proportions of 27 ounces by moasure: the 27 ounces of hydrogon would bo found to weigh 1 grain, and the 27 ounces of oxygen to weigh 16 grains.

Thus the two groat facts or laws respecting chemical compounds which Dalton laid down, by ascortaining the exact weights in which bodies combine, Gay-Lussac confirmod by experimonts on tho oxact volumos in which elomonts combine. Further, Gay-Lussac's experiments and Avogadro's reasoning strongly supportod Dalton's theory of atoms.

RECAPITULATION.

What are atomic weights or combining weights? First, they are represented by the smallest portion (relative to 1 part of hydrogen) in which an element migrates from compound to compound. Thus 1 part by weight of hydrogen can be eliminated from 18 similar parts of water by action of certain metals, leaving 1 of hydrogen and 16 of oxygen combined with the metal. From the latter compound 1 more of hydrogen is eliminated by a second experiment with more metal, leaving 16 of oxygen combined with the metal. In these and other well-known reactions, 16 parts of oxygen take part in the various operations; 16, therefore, is the probable atomic weight of oxygen; and so with other elements and radicals. Secondly, the weight of the atoms, or the atomic weights, of the gaseous elements already studied, must differ from each other to the extent that equal volumes of those elements differ in weight. For equal volumes contain an equal number of molecules equal in size (Avogadro and Ampère), and each molecule *of an element* is composed of two atoms; so that equal volumes of the gaseous elements contain an equal number of atoms. Now, bulk for bulk, chlorine is thirty-five and a half (35·5) times as heavy as hydrogen; so that the molecule of chlorine must be 35·5 times the weight of the molecule of hydrogen. And as the molecules of chlorine and hydrogen contain two atoms each, the atom of chlorine must be 35·5 times as heavy as that of hydrogen. The actual weight of atoms can never be ascertained; but that is of little consequence if we can only determine, with exactitude, their comparative weights. Comparing, then, all atomic weights (sometimes obscurely termed *equivalents*) with each other, and selecting hydrogen as the standard of comparison (because it is the lightest body known, and therefore, probably, will have the smallest atomic weight), and assigning to it the number 1, we see that the atomic weight of chlorine will be represented by the number 35·5. By parity of reasoning the atomic weight of oxygen is 16; for oxygen is found, by experiment, to be 16 times as heavy as hydrogen. Similarly the atomic weight of nitrogen is found to be 14. The atomic weight of carbon is 12,—not because its vapour has been proved to be 12 times as heavy as hydrogen, for it has never yet been converted into the gaseous state, but because no gaseous compound of carbon which has been analysed has been found to contain in *two* volumes (1 of which, if hydrogen, would weigh 1 part) less than 12 parts of carbon. (For an explanation of this reference to *two* volumes see next page.)

By thus weighing equal volumes of gaseous elements, or equal volumes of gaseous compounds of non-volatile elements, and ascertaining by analysis the proportion of the non-volatile element, whose atomic weight is being sought, to the volatile element, whose atomic weight is known, the atomic weights of a large number of the elements have been determined. Some of the elements, however, do not form volatile compounds of any kind; the stated atomic weights of these elements, therefore, are at present simply the proportions by weight in which they combine with or displace elements whose atomic weights have been determined, the proportions being in most cases checked by isomorphic considerations, and the relation of the element to other forces, especially heat.* (*Vide infra.*)

Molecular Weight and Molecular Volume.

The weight of a molecule is simply the sum of the weights of its atoms; thus—

$$H_2 = 2,\ O_2 = 32,\ Cl_2 = 71,\ H_2O = 18,\ HCl = 36{\cdot}5.$$

The foregoing formulæ are *molecular formulæ* or *two-volume formulæ*. It will be remembered that one volume of hydrogen and one of chlorine gave *two* of hydrochloric acid, and that two of hydrogen and one of oxygen gave *two* of steam, etc.

Molecular Volume.—If the quantities just mentioned be weighed out (in grains or other weights), or if the molecular weights of any gases or liquids be taken and exposed to similar (high) temperatures and pressures, *they will be found*

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* *Isomorphous* bodies (*ἴσος, isos,* equal, and *μορφή, morphē,* form) are those which are similar in the shape of their crystals. This identity in crystalline form is so commonly associated with similarity of constitution, that non-crystalline substances resembling each other in structure are often regarded as isomorphous. When one element unites with another in more than one proportion, and its atomic weight is so far uncertain, the isomorphism of either of its compounds with some other compound of known constitution is usually accepted as evidence of some value as to which proportion is atomic, especially if the compounds are so closely isomorphous that a crystal of either will "grow" in a solution of the other. The specific heat of elements will be treated of subsequently.

to occupy the same volume. Conversely, if equal volumes of gases or vapours be measured out, and then the whole weighed, the resulting figures (all referred to 2 of hydrogen as a starting-point or standard) are the molecular weights of the respective substances. For, equal volumes contain equal numbers of molecules (Avogadro). Why? Because equal volumes have equal physical properties (Boyle, Charles); and various things which have similar properties are by that fact shown to be similar things—the mode of reasoning which from childhood onward teaches us that two separate things (*e.g.* two pennies) are similar things. In the cases now being considered, the things differ *chemically*, for they have entirely different chemical properties; they are not similar chemically: the point is, that having similar *physical* properties, they are similar *physically*; whatever the number of molecules in a volume of one of the gases or vapours, there must be a similar number in similar volumes of the others, therefore *the differences in the weights of tangible volumes are the differences in the weights of the intangible molecules.* This subject will again be referred to in connection with quantitative analysis, *vide Index* "Molecular Weight"; at present the following illustration will suffice. A volume of hydrogen (about 54 fluid ounces) which, at a temperature of, say 300° F. or 400° F., and common atmospheric pressure, would weigh 2 grains, would, in the case of vapour of water (steam), weigh 18 grains. Hence we are justified in considering, indeed compelled to consider, the molecule of water to contain two atoms of hydrogen (=2) and one of oxygen (=16), and its formula to be H_2O (=18), and not H_4O_2, in which case its vapour would be twice as heavy as it really is found to be.

Construction of Formulæ.—The composition of hydrochloric acid (HCl), water (H_2O), ammonia gas (NH_3), carbonic acid gas (CO_2), or any other compound, as well as the weight of an element that may be concerned in its formation, cannot be ascertained by actual experiment until the student is far advanced in practical chemistry—until he is able to *analyse* not only *qualitatively*, but, by help of a balance, *quantitatively.* The percentage composition of a chemical substance having been determined by quantitative analysis, its formula is constructed by the aid of the foregoing and other theoretical considerations. The correctness of such formulæ can be verified by expert analysts, but must be taken for granted by learners. This subject will again be referred to in the latter part of this Manual.

QUANTIVALENCE OF ATOMS, OR VALENCY.

Turning from the *weights* of atoms, their chemical *value* may now be considered, or their *quantivalence*. The exchangeable chemical value of atoms in relation to each other may be compared to the exchangeable commercial value of coins. As compared with a penny, a groat is four-valued; as compared with hydrogen, carbon is quadrivalent. Here again hydrogen is conventionally adopted as the standard of comparison. An oxygen atom in its relations to an atom of hydrogen is bivalent (biv′-a-lent; of double worth, from *bis*, twice, and *valens*, being worth); an atom of it will displace two atoms of hydrogen, or combine with the same number; nitrogen is usually trivalent (triv′-a-lent; from *tres*, three, and *valens*); while the carbon is quadrivalent (quad-riv′-a-lent; from *quatuor*, four, and *valens*). Chlorine, iodine, and bromine, as well as potassium, sodium, and silver among the metals, are, like hydrogen, univalent (u-niv′-a-lent; from *unus*, one, and *valens*). Barium, strontium, calcium, magnesium, zinc, cadmium, mercury, and copper, like oxygen, are bivalent. Phosphorus, arsenium, antimony, and bismuth, like nitrogen, usually exhibit trivalent properties; but the composition of certain compounds of these five elements shows that the several atoms are sometimes quinquivalent (quin-quiv′-a-lent; *quinquies*, five times, and *valens*). Gold and boron are trivalent. The atoms of silicon (the characteristic element of flint and sand), tin, platinum, and lead resemble carbon in being quadrivalent. Sulphur, chromium, manganese, iron, cobalt, and nickel are sexivalent (sex-iv′-a-lent; from *sex*, six, or *sexies*, six times, and *valens*), but frequently exert only bivalent, trivalent, or quadrivalent activity. This *quantivalence* (quant-iv′-a-lence; from *quantitas*, quantity, and *valens*), also termed *atomicity* (maximum quantivalence), *dynamicity*, *equivalence*, and, simply, *valency*, of atoms, may be ascertained at any time on referring to the Table of the Elements at the end of this volume, where Roman numerals, I, II, III, IV, V, VI, are attached to the symbols of each element to indicate atomic univalence, bivalence, trivalence, quadrivalence, quinquivalence, or sexivalence. Dashes (H', O'', N''') similar to those used in accentuating words are often used instead of figures in expressing quantivalence. The quantivalence of elements, as they one after another come under notice, should be carefully committed to memory; for the composition of compounds can often be thereby predicated with accuracy, and remembered with ease. For instance, the hydrogen compounds of chlorine, Cl', oxygen, O'', nitrogen, N''', and carbon, C'''', will be respectively $H'Cl'$, H'_2O'', H'_3N''', and H'_4C'''',—one univalent atom, H, balancing or saturating one univalent atom, Cl'; two univalent atoms, H'_2, and one bivalent atom, O'', saturating each other; three univalent atoms, H'_3, and one atom having trivalent activity, N''', saturating each other; and four univalent atoms, H'_4, and one quadrivalent atom, C'''', saturating each other. Carbonic acid gas, $C^{iv}O''_2$, again, is a saturated molecule containing, in one molecule, one quadrivalent and two bivalent atoms.

The subject of quantivalence will be further explained after the first six metals have been studied, when abundant illustrations of quantivalence will have occurred.

DEFINITIONS.

Chemistry is the study of the force by which matter becomes permanently altered in properties.

The Chemical Force, like other forces, cannot itself be described, for, like them, it is only known by its effects. It is distinguished from other forces by the facts that (*a*) it produces an entire change of properties in the bodies on which it is exerted, and that (*b*) it is exerted only between definite weights and volumes of matter. Like *the force of cohesion*, which is the name given to the attraction which molecules have for each other, and which is great in solids, small in liquids, and apparently absent in gases; and like *the force of adhesion*, which is the name given to the attraction which a mass of molecules has for another mass, *the chemical force* acts only within immeasurable distances; indeed, inasmuch as the chemical force appears to reside in atoms, that is to say, is exerted inside a molecule, while all other forces affect entire molecules, the chemical force may be said to be distinguished (*c*) by being exerted within a smaller distance than that at which any other force is exerted.

An Element is a substance which cannot by any known means be resolved into any simpler form of matter.

An Atom of any element is a particle so small that it undergoes no further subdivision in chemical transformations.

A Molecule is the smallest particle of matter that can exist in a free state.

A mere mixture of substances is one in which each ingredient retains its properties.

A Chemical Compound is one in which definite weights of constituents have undergone an entire change of properties. A "compound" *in pharmacy* is an intimate mixture of substances, but still only a mixture: it is not a *chemical* compound; the ingredients have not entered into *chemical* union or combination.

Combustion is a variety of chemical combination; a variety in which the chemical union is sufficiently intense to produce heat and, generally, light.

The Law of Diffusion is one under which gases mix with each other at a rate which is in inverse proportion to the square roots of their relative weights; that is, irrespective of, and even in spite of, their comparative lightness or heaviness.

A Chemical Symbol is a capital letter, or a capital and one small letter. It has four functions, namely—

1. It is shorthand for the *name* of the element.
2. It represents one *atom* of the element.
3. It stands for a constant *weight* of the element—the atomic weight or combining weight.
4. Symbols represent equal and *single volumes* of gaseous elements.

A Chemical Formula represents (1) *a molecule* either of an element or of a compound. It has four other functions—

2. It indicates at a glance the *names* of the elements in the molecule.
3. Its symbol, or symbols, together with a small figure attached to the foot of any symbol, show the *number of atoms* in the molecule.
4. It stands for a constant weight of a compound—the molecular weight—the sum of the combining *weights* or of the weights of the atoms in the molecule.
5. It represents *two volumes* of the substance (if volatilizable) in the state of gas or vapour, and the

number of volumes of gaseous elements from which two volumes of any gaseous compound were obtained.

A Chemical Equation or *a Chemical Diagram* is a collection of formulæ and symbols so placed on paper as to form a picture or illustration of the state of things before and after that *metathesis* (interchange) of atoms of molecules which results in the formation of molecules of new substances.

A Solid is a substance the molecules of which are more or less immobile, though probably not in absolute contact.

A Liquid is a substance the molecules of which so freely move about each other that it readily assumes and retains the form of any vessel in which it is placed.

A Gas is a substance the molecules of which are so far apart that they seem to have lost all attraction for each other, and, indeed, to have acquired the property of repulsion to such an extent that they are only prevented from receding to a still greater extent by the pressure of surrounding matter. Motion is especially characteristic of the molecules of gaseous fluids.

The Two Laws regulating Chemical Combination (either by weight or volume).

First. The Law of Definite Proportions. A definite compound always contains the same elements and the same proportions of those elements—by weight or by volume.

Second. The Law of Multiple Proportions. When two elements unite in more than one proportion, by weight or by volume, they do so in simple multiples of that proportion forming *different* compounds, each of which, as regards definiteness of composition, of course obeys the first law.

Reciprocal Proportions. The proportions in which two elements unite with a third, are the proportions in which they unite with each other.

Atomic Weights are, first, the proportions in which elements are found to combine with each other by weight. (The figures showing these proportions are purely relative; but all chemists agree to make this relation fixed by giving the number 1 to hydrogen.) Secondly, they are the weights of equal volumes of gaseous elements (relative to one of hydrogen).

Molecular Weights.—These are the weights of equal volumes of gases or vapours, under equal circumstances of temperature and pressure, and relative not to 1 but to 2 of hydrogen. In the case of non-volatile bodies molecular weight is deduced from the observed analogies of the bodies with those whose molecular weight admits of proof.

Quantivalence of Atoms.—The chemical value for work of an atom—relative to one of hydrogen. (*Caution.* Quantivalence gives no clue to that varying intensity of union of atoms which results in varying stability of compounds.)

THE LEARNER IS RECOMMENDED TO READ THE FOREGOING PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY CAREFULLY ONCE OR TWICE, THEN TO STUDY (EXPERIMENTALLY, IF POSSIBLE) THE FOLLOWING PAGES, RETURNING TO AND READING OVER THE GENERAL PRINCIPLES FROM TIME TO TIME, UNTIL THEY ARE THOROUGHLY COMPREHENDED.

Minor principles of Chemical Philosophy will be found scattered throughout the following pages. (Also *vide* Index, under the word "Principles.")

Students of pure Chemistry, especially when fairly well acquainted with chemical facts, will also find the principles of Chemistry, including the probable constitution as distinguished from the mere composition of chemical substances, fully set forth in the larger text-books.

QUESTIONS AND EXERCISES.

What do you understand by *chemical* action? Give examples.—How is the chemical force distinguished from other forces?—Adduce evidence that elements exist in compounds; that sulphide of iron, for instance, still contains particles of sulphur and iron, though it possesses properties so different from those elements.—Define the term "atom."—What condition is essential for the manifestation of chemical force?—Can an atom exist in an uncombined state? and when are atoms most potent to enter into chemical combination?—What is a molecule?—How may the results of chemical reactions be expressed on paper?—Enumerate the functions of a symbol.—Give the additional functions of a chemical formula.—Describe by a diagram or an equation the reaction which ensues when red-hot charcoal is plunged into oxygen gas.—Draw diagrams representing the formation of P_2O_5, SO_2, and FeI_2, respectively.—Enumerate the differences in the physical conditions of the molecules in a solid, a liquid, and a gas.—State the law of constant proportions.—State the law of multiple proportions.—State the principle of reciprocal proportions.—Give illustrations of the above laws.—Describe the origin and use of the atomic theory.—What do you understand by the atomic weight and the molecular weight of an element?—Representing the weight of an atom of hydrogen as 1, what will be the atomic weights of carbon, sulphur, nitrogen, and iodine? Give reasons for considering the stated weights to be correct.—In what proportion, by volume, do elements in the gaseous state chemically combine?—What relation exists between the combining volumes of elements in the gaseous state and their atomic weights? Give the explanation for this. Is there any difference between the molecular volumes of simple and of compound gases?—Define isomorphism.—Explain the value of isomorphism as evidence of atomic weight. What is to be understood by the quantivalence of atoms? Give examples of univalent, bivalent, trivalent, and quadrivalent atoms.—How may the quantivalence of an element be expressed in its atomic symbol.—Give formulæ in which the quantivalence of one atom is saturated by the combined quantivalence of others.

The reader is also recommended to question himself, or be questioned, on the " definitions " given on pages 57 to 60.

THE ELEMENTS AND THEIR COMPOUNDS.

Having thus obtained a general idea of the nature of such elements as have special interest for the medical and pharmaceutical student, and which indeed are all with which any student of chemistry should at present occupy his attention, we may pass on to consider in detail the relations of the elements to each other. The elements themselves, in the free condition, are seldom used in medicine, being nearly always associated—bound together by the chemical force; in this combined condition, therefore, they must be studied, inorganic combinations first, organic afterwards. Most compounds met with in the mineral kingdom may be regarded as containing two parts or roots, two radicals:—the one usually metallic, or, to speak more generally, basylous; the other commonly a non-metallic, simple or complex, acidulous radical. In the following pages the basylous radicals, or metals, will be considered first, the acidulous radicals afterwards. (Then will follow the chemistry of compounds, many of which have not so simple a constitution as that just indicated.) Each radical will be studied from two points of view, the synthetical and the analytical; that is to say, the properties of an element on which the preparation of its compounds depends will be illustrated by descriptions of actual experiments, and thus the principles of chemistry and their applications to medicine and pharmacy be simultaneously learnt; then the reactions by which the element is detected, though combined with other substances, will be performed, and so the student be instructed in qualitative analysis. Synthetical and analytical reactions are, in truth, frequently identical, the object with which they are performed giving them synthetical interest on the one hand, or analytical interest on the other.

A good knowledge of chemistry may be acquired synthetically by preparing considerable quantities of the salts of the different metals, or analytically by going through a course of pure qualitative analysis. But the former plan demands a larger expenditure of time than most students have to spare, while under the latter system pupils generally lose sight of the synthetical interest which attaches to analytical reactions. Hence the more useful system, now offered, of studying each metal, etc., from both points of view, time being economized by the operator preparing only small specimens of compounds.

Chemical synthesis and analysis, thoughtfully and conscientiously followed, without hurry and mere superficial consideration, but, of course, without undue expenditure of time, will insensibly carry the principles of chemistry into the mind, and fix them there indelibly.

Note.—As a general rule, throughout this Manual paragraphs describing experiments to be performed are distinguished from paragraphs containing matter merely to be read by being printed in somewhat more widely spaced type.

Elements and their Atomic Weights, etc.—For an alphabetical list see the two pages immediately preceding the Index at the end of this volume.

THE BASYLOUS RADICALS.

POTASSIUM.

Symbol, K. Atomic weight, 39.
Formula, K_2. Probable molecular weight, 78.

Memoranda.—The chief sources of the potassium salts * are the chloride found at Stassfurt, in Prussia, as the mineral *Carnallite* ($KCl, MgCl_2, 6H_2O$); *Kainite*, a double sulphate of potassium and magnesium with magnesium chloride, also occurring among the Stassfurt minerals; the nitrate found in soils, especially in warm countries; and the compounds of potassium existing in plants. The vegetable salts of potassium are converted into carbonate (other salts are present) when the wood or other parts are burned to ashes. If the ashes be lixiviated with water, and the solution evaporated to dryness, the residue when fused constitutes *crude potashes*. The residue calcined on the hearth of a reverberatory furnace till white, gives the product termed *pearlash*, or impure carbonate of potassium. Large quantities of carbonate are thus produced in North America and Russia, and, latterly, from the sugar beetroot marc in France. From the native chloride, and from the carbonate purified "by treating the pearlash with its own weight of distilled water, filtering, and evaporating the solution so formed just to drynoss, while it is kept briskly agitated" (*Potassii Carbonas*, B.P., "K_2CO_3, with about 16 per cent. of water of crystallization"), nearly all other compounds of potassium are made. Exceptions occur in cream of tartar (*Potassii Tartras Acida*, B.P.), which is the moro or less purifiod natural potassium salt of the grape vine, and in nitrate of potassium. Potassium is a constituent of between forty and fifty chemical or galenical preparations of the British Pharmacopœia.

Carbonate of potassium (*Potassii Carbonas*, B.P.), the old carbonate of potash, is a white crystalline or granular powder, insoluble in alcohol, very soluble in water, rapidly liquefying in the air through absorption of moisture, alkaline and caustic to the taste. It loses all water at a red heat.

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* The ill-defined term *salt* includes most solid definite chemical substances, but more especially those which assume a crystalline form.

Preparation.—Potassium itself is isolated with some difficulty by distilling a mixture of its carbonate and charcoal, or by Castner's method (see Sodium). It rapidly oxidises in the air, hence is always kept below the surface of mineral naphtha, a liquid containing no oxygen. It crystallizes in octahedra.

Quantivalence.—The atom of potassium is univalent, K′.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Synthetical Reactions.*

These are utilized in making preparations of potassium. The word *synthesis* is from σύνθεσις (*sunthĕsis*), a putting together; *analysis* from ἀναλύω (*analuō*), to resolve.

Hydrate of Potassium. Caustic Potash.

First Synthetical Reaction.—Boil together, for a few minutes, in a basin, five or six grains of carbonate of potassium (K_2CO_3) and a like quantity of slaked lime (Ca2HO) with a small quantity of water. Set the mixture aside till all solid matter has subsided.

This liquid is a solution of caustic potash, or hydrate of potassium (KHO). Made of a prescribed strength, nearly 6 per cent., it forms the *Liquor Potassæ*, B.P.

The mixture is known to be boiled long enough when a little of the clear liquid, poured into a test-tube and warmed, gives no effervescence on the addition of an acid (sulphuric, hydrochloric, or acetic)—a test whose mode of action will be explained hereafter.

Best method of expressing decompositions.—This will be easy of comprehension, if what has already been stated concerning symbols and formulæ on pp. 35 to 37 and 42 and 43 has been carefully and thoughtfully considered. The best means of showing on paper the action which occurs when chemical substances attack each other, is by the employment either of equations or diagrams, setting forth the formulæ of the molecules concerned in the reaction. In an *equation* the formulæ of the salts used are written on one line, the sign of addition (+) intervening;

the sign of equality (=) follows, and then the formulæ of the salts produced, also separated by a plus sign (+). Thus :—

$$K_2CO_3 + Ca2HO = 2KHO + CaCO_3.$$

In this reaction (the operation just performed) the metals of (the molecules of) the two salts change places : from K_2CO_3 and Ca2HO there are produced $CaCO_3$ and KHO (two molecules, 2KHO); from carbonate of potassium and hydrate of calcium there result carbonate of calcium (the insoluble portion) and hydrate of potassium (in solution).*

In constructing a *diagram* or pictorial illustration of a chemical reaction (the reaction, for instance, just described), *first* the formulæ of the salts used are written under each other on the left side of the leaf of a note-book, thus :—

K_2CO_3

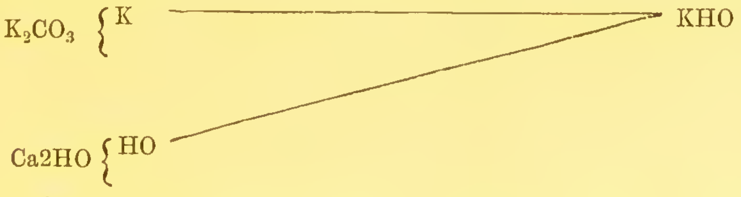
Ca2HO

Such formulæ are, in this Manual, always given with the description of the reaction. *Secondly*, on the right is then written the formula of the chief substance produced, thus :—

K_2CO_3 KHO

Ca2HO

Thirdly, the formation of this chief body under consideration—that is to say, both the origin of its elements and their destination—is traced out by the help of brackets and letters (which show the source of the elements) and converging lines (which suggest the approach and final union of those elements) thus :—



For the next stage (at other stages, perhaps, in other reactions) the reader's own intelligent power of thought and reflection *must* come into exercise. He *must* reason somewhat as follows: "I am converting, and entirely converting, a quantity of carbonate of potassium into hydrate of potassium. A molecule, the smallest quantity I can picture on paper, of the carbonate of potassium (K_2CO_3) contains, I am told, two atoms of potassium (K_2), and a molecule of the hydrate (KHO) one atom (K). Therefore—*therefore*—each molecule of the carbonate (K_2CO_3) will furnish *two* molecules of the hydrate (2KHO). Moreover I notice that in the formula of a molecule of the hydrate of calcium (slaked lime) I employ, there are 2 of the HO (that is 2HO); and this fact confirms me in the deduction that one molecule of the carbonate affords *two* molecules of the hydrate." The pupil will then amend his diagram thus:—

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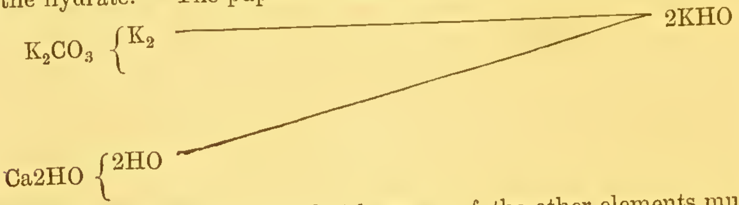
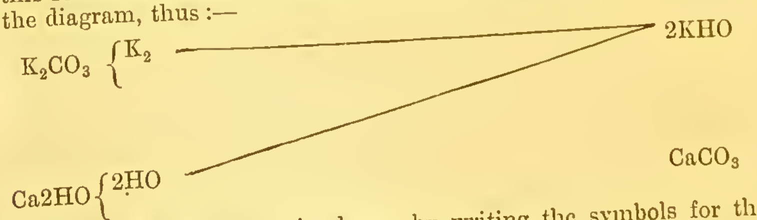
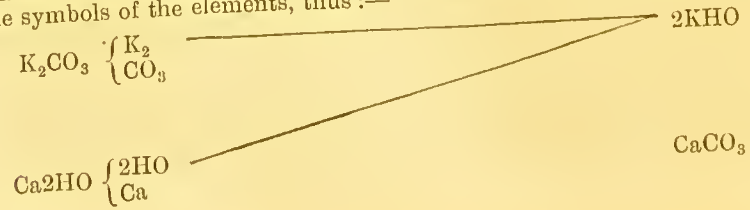
* If the student is already accustomed to the use of ordinary equations, he may pass on to Note 1, on p. 67 ; if not, the author would strongly recommend the temporary employment of diagrams for expressing chemical changes. Indeed, the occasional use of graphic equations or diagrams is of advantage to all students. For while an equation or a diagram equally well records the formulæ of the salts concerned in the whole reaction, the diagram alone suggests the *mode* in which its writer believes the respective atoms to change their positions.—In the paragraphs succeeding the above, detailed explanations are given respecting the use and construction of diagrams.



Fourthly, the question as to what becomes of the other elements must be cleared up. Indeed, when the reader remembers that he is studying this reaction for the aid it affords him in learning chemistry, and not because he is desirous of manufacturing caustic potash, he will see that this latter part of the reaction is quite as important as the former. To complete the diagram, then, he must first know what other compound is produced, and its formula. The context of his Manual will afford this information. In this case carbonate of calcium is produced ($CaCO_3$). (This product is, in fact, precipitated chalk, together with any excess of slaked lime and any natural impurities in the slaked lime. *Pure* "precipitated chalk" is made by an analogous reaction described subsequently.) The source of the elements of the carbonate of calcium, and, finally, their union must be indicated just as the source and mode of formation of the potash were indicated. That is to say, after the formula of this second substance produced ($CaCO_3$) is written on the right hand of the diagram, thus:—



the source of its elements is shown by writing the symbols for those elements on the right of the bracket attached to the formula containing the symbols of the elements, thus:—



Radicals.—The above elements and compounds are termed *radicals*, each being the common *root* (*radix*) in a series of salts. Why compound radicals (as NO_3, SO_4, PO_4, etc.) differ in quantivalence need not be fully explained at present. Their constituent atoms doubtless always exert the same amount of attractive force, nearly but not quite all this force being exerted in retaining the atoms in one group, and the remainder probably determining the quantivalence. Compound radicals are more or less stable groups of atoms, capable of migration without change, but not necessarily capable of existing in the free state.*

Liquor Potassæ is officially directed to be made as follows † :—

Dissolve 1 pound of carbonate of potassium in 1 gallon of water; heat the solution to the boiling point in a clean iron vessel, gradually mix with it 12 ounces of washed slaked lime (obtained from about 13 ounces of slaked lime washed with distilled water until a little of the washings, acidified with nitric acid, gives no cloudiness with nitrate of silver), and continue the ebullition for ten minutes with constant stirring. Then remove the vessel from the fire; and when, by the subsidence of the insoluble matter, the supernatant liquor has become perfectly clear, transfer it by means of a siphon or by decantation to a green-glass bottle furnished with an air-tight stopper, and add distilled water, if necessary, to make it correspond with the tests of *specific gravity* and *neutralizing power*. (These tests and the modes of applying them will be explained in subsequent sections.)

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* Some modern chemical authors term these roots *radicles*, a word more usefully expressive of little roots or rootlets. The word *radicle* is indeed thus used as a diminutive in botany.

† The official processes will not usually be reprinted in this Manual, belonging, as they do, more to the manufacturing than to the educational side of practical chemistry. But pupils should take care that they *understand* every word of the processes, whether as regards chemical or mechanical details; the medical student in order that he may learn chemical principles—the principles on which the successful practice of modern medicine depends—the pharmaceutical student in order that he too may know the principles on which his avocation largely depends, and in order that he may apply those principles in his pursuit of that avocation. With such views before him, each student should carefully read through the above process; and, in future, after making an officially interesting synthetical experiment, should turn to the corresponding monograph in his Pharmacopœia and assure himself that he *understands* all that is there stated.

Solid Potash.—Solution of potash evaporated to dryness in a silver or clean iron vessel, and the residue fused and poured into moulds, constitutes *Potassa Caustica*, B.P. It often contains chlorides, detected by nitrate of silver, and sulphates, detected by a barium salt, as described subsequently in connection with hydrochloric and sulphuric acids.

Sulphurated Potash.

Second Synthetical Reaction.—Into a test-tube put a few grains of a mixture of *previously dried* carbonate of potassium with half its weight of sulphur. Heat the mixture gradually until it ceases to effervesce. The resulting fused mass poured on a slab and quickly bottled is the *Potassa Sulphurata*, Sulphurated Potash, of the British Pharmacopœia.

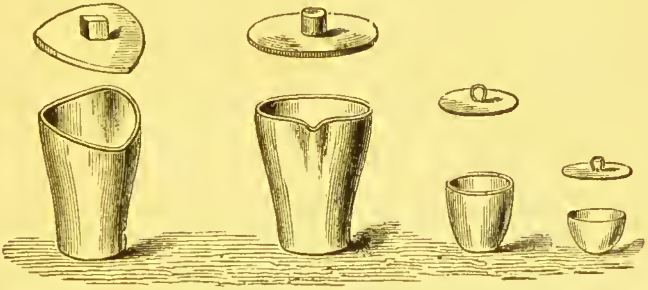
$$\underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{3K_2CO_3} + \underset{\text{Sulphur.}}{4S_2} = \underset{\substack{\text{Hyposulphite}\\\text{of potassium.}}}{K_2S_2O_3} + \underset{\substack{\text{Sulphide of}\\\text{potassium.}}}{2K_2S_3} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

As met with in pharmacy, this salt is not a single definite chemical compound, but a mixture of several; in short, its chemical character is well indicated by its vague name. When fresh, and if carefully prepared with the official proportions of dry ingredients, it is of the colour of liver (whence the old name "liver of sulphur"), and consists, as shown by J. Watts, of the salts mentioned in the foregoing equation, together with a little undecomposed carbonate of potassium, with perhaps higher sulphides of potassium (K_2S_4 and K_2S_5); but, rapidly absorbing oxygen from the air, it soon becomes green and yellow, sulphite (K_2SO_3) and sulphate of potassium (K_2SO_4) are successively formed, and ultimately a useless mass of a dirty white colour results, consisting of sulphate and hyposulphite, with generally some carbonate of potassium and free sulphur. Moreover, if overheated in manufacture, the hyposulphite $4(K_2S_2O_3)$ is decomposed into sulphate $3(K_2SO_4)$ and sulphide (K_2S_5) of potassium. Recently made, about fifty per cent. should be soluble in rectified spirit. It is occasionally employed in the form of ointment (*Unguentum Potassæ Sulphuratæ*, B.P.)

The extremely, indeed most unusually, complicated nature of the decomposition will probably cause failure in any attempt by a student to draw out an equation or a diagram of the reaction without the aid of the printed equation given above. He may therefore content himself, in this case, by introducing into his note-book a diagram founded directly on the equation, and on the numbers of molecules there stated. With this printed equation, and the details of construction of diagrams given in connection with the first synthetical reaction, he will be able to give a diagram of this second synthetical reaction without unduly troubling his reasoning powers, while at the same time he will be familiarizing himself with the more mechanical portions of the diagram.

In preparing large quantities of sulphurated potash, the test-tube is replaced by an earthenware vessel termed a *crucible* (possibly from *crux*, a cross, for originally a cross was impressed upon the melting-pot as used by alchemists and goldsmiths: others derive the word from *crux*, an instrument of torture, the sense here being symbolical).

Fig. 12. *Fig.* 13. *Fig.* 14.



CRUCIBLES OF VARIOUS FORMS.

Heating crucibles.—Crucibles of a few ounces' capacity may be heated in an ordinary grate-fire. Larger ones require a stove with a good draught—that is, a *furnace*. Even the smaller ones are more conveniently and quickly heated in a furnace. Half-ounce or one-ounce experimental porcelain crucibles may be heated in a spirit- or gas-flame; the air-gas flame already described being generally the most suitable.

Acetate of Potassium.

Third Synthetical Reaction.—Place ten, twenty, or more grains of carbonate of potassium in a small dish, and *saturate* (*satur*, full) with acetic acid; that is, add acetic acid so long as effervescence is thereby produced; the resulting liquid is a strong, slightly acid solution of acetate of potassium. Evaporate most of the water in an open dish (*see* figs. 15 & 16, p. 73), stirring with a glass rod * to promote evolution of vapour; a white salt remains, which fuses on the further careful application of heat: this is the official Acetate of Potassium (*Potassii Acetas*, B.P.), formerly termed Acetate of Potash. If fused in the open vessel, the acetate is liable to become slightly charred and discoloured; this is prevented by transferring the solid residue to a test-tube or Florence flask before finally fusing. It forms a white deliquescent foliaceous satiny mass, neutral to test-paper, and wholly soluble in spirit. A ten per cent. solution in water forms the "Solution of Acetate of Potassium," B.P.

$$\underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{K_2CO_3} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{2HC_2H_3O_2} = \underset{\substack{\text{Acetate of}\\\text{potassium.}}}{2KC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Explanation of formulæ.—The formula for one molecule of acetic acid (the acetate of hydrogen) is $HC_2H_3O_2$, and one of acetate of potassium $KC_2H_3O_2$. The grouping, $C_2H_3O_2$, is characteristic of all acetates; it is univalent.

Explanation of process.—When two molecules of acetic acid ($2HC_2H_3O_2$) and one of carbonate of potassium (K_2CO_3) react, two molecules of acetate of potassium ($2KC_2H_3O_2$) and one of carbonic acid (H_2CO_3) are produced, the latter at once splitting up into water (H_2O) and carbonic acid gas (CO_2), as already shown in the equation.

Diagram of the reaction.— The nature of the above operation is indicated by an *equation*; it (and succeeding reactions) should be expressed in the student's note-book as a *diagram*, and, if possible, without the aid of the above equation.

Note.—The foregoing reaction has a general as well as a special synthetical interest. It represents one of the commonest methods of forming salts, namely, the saturation of a carbonate by an acid, or *vice versâ*. Carbonates added to acetic acid yield acetates, to nitric acid nitrates, to sulphuric acid sulphates. Many illustrations of this general process occur in pharmacy.

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* Glass rod is usually purchased in the form of long sticks. The pieces may be cut to convenient lengths of from 6 to 12 inches (*vide* p. 5), sharp ends being rounded off by holding the extremity in a flame for a few minutes.

Evaporation of water from a liquid is best conducted in wide shallow vessels rather than in narrow deep ones, as the steam can thus quickly diffuse into the air and be conveyed rapidly away; hence a small round-bottomed basin, heated as shown in fig. 15, is far more suitable than a test-tube for such operations. On the manufacturing scale, iron, or iron lined with enamel, or semiporcelain, copper, tinned copper, or solid tin pans are used. Up to 12 or 18 inches diameter, pans, basins, or dishes made of Wedgwood ware or porcelain composition (fig. 16), may be employed. Small dishes may be supported by retort stands (fig. 15), larger by cylinders (fig. 16) to which the dish is, if less in diameter than the cylinder, adapted by such flat rings or diaphragms as are shown in the figure.

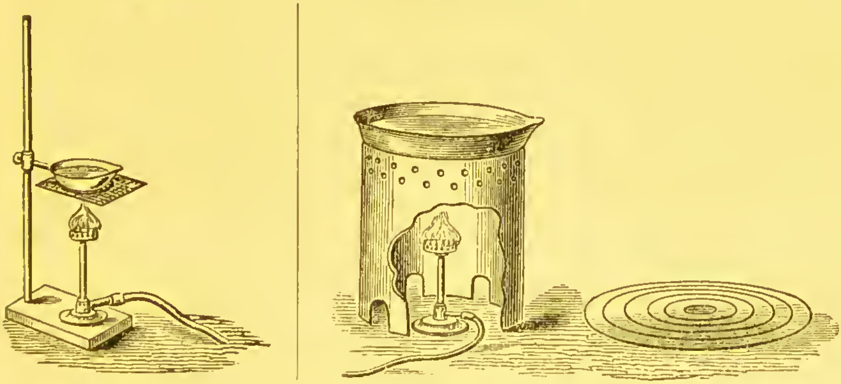

Fig. 15. *Fig.* 16.

EVAPORATION FROM SMALL AND LARGE BASINS.

Bicarbonate of Potassium.

Fourth Synthetical Reaction.—Make a *strong* solution of carbonate of potassium by heating in a test-tube a mixture of several grains of the salt with rather less than an equal weight of water. Through the cool solution pass carbonic acid gas, slowly but continuously; after a time a white crystalline precipitate of Acid Carbonate or Bicarbonate of

Potassium ($KHCO_3$) of the Pharmacopœia (*Potassii Bicarbonas*, B.P.), will be formed—the old Bicarbonate of Potash.

K_2CO_3	+	H_2O	+	CO_2	=	$2KHCO_3$
Carbonate of potassium.		Water.		Carbonic acid gas.		Bicarbonate of potassium.

The carbonic acid gas for this operation is economically and conveniently prepared from small lumps of marble, though it might be obtained from any carbonate; thus the previous synthetical reaction could be made available for this purpose, the carbonic acid gas evolved on the addition of the acetic acid to the carbonate of potassium being conducted into a strong solution of more carbonate of potassium by a glass tube bent and fitted as described when treating of oxygen gas. Economy also causes hydrochloric acid to be used in preference to acetic or any other acid.

Generate the carbonic acid gas by adding common hydrochloric acid, diluted with twice its bulk of water, to a few fragments of marble contained in a test-tube or small flask, and conduct the gas into the solution of carbonate of potassium by a glass tube bent to a convenient angle or angles and fitted to the test-tube by a cork in the usual way (*see* fig. 10, p. 20, though no heat is necessary). The tube may be replenished with marble or acid, or both, when the evolution of gas is becoming slow. In working on any larger quantity than a few grains of the carbonate a wide delivery-tube should be employed, or the end of the narrow tube occasionally be cleared from any bicarbonate that may have been deposited in it. A more economical arrangement of the apparatus employed in this process will be described under the corresponding sodium salt (p. 88).

Deposition of the bicarbonate explained.—Bicarbonate of potassium is to a certain extent soluble in water; but as it is less so than the carbonate of potassium, and as a *saturated* solution of the latter has been used, a precipitation of a part of the bicarbonate inevitably occurs. In other words, the quantity of water present is sufficient to keep the carbonate, but insufficient to retain the equivalent quantity of bicarbonate in solution.

Properties.—Prepared on the large scale, bicarbonate of potassium occurs in colourless, non-deliquescent right rhombic prisms; it has a saline, feebly alkaline, non-corrosive taste. Heated to redness, it loses 31 per cent. of its weight, and is converted into carbonate (K_2CO_3), water (H_2O), and carbonic acid gas (CO_2).

$$\begin{array}{ccccccc} \underbrace{2KHCO_3} & = & \underbrace{K_2CO_3} & + & \underbrace{H_2O} & + & \underbrace{CO_2} \\ 2)\underline{200} & & 2)\underline{138} & & 2)\underline{18} & & 2)\underline{44} \\ 100 & = & 69 & + & 9 & + & 22 \end{array}$$

The foregoing equation and accompanying molecular weights (*see* page 54) show how bicarbonate of potassium, the molecular weight of which happens to be 100, *must* lose 31 per cent. (9 + 22) when completely decomposed by heat.

Effervescing solution of potash.—A solution of 30 grains of this bicarbonate in one pint of water, charged with 5 times its bulk of carbonic acid gas by pressure, is medicinal "potash water," *Liquor Potassæ Effervescens*, B.P.

Notes on Nomenclature.—The prefix *bi-* in the name "bicarbonate of potassium," serves to recall the fact that to a given amount of potassium this salt contains *twice* as much carbonic radical as the carbonate. The salt is really a "carbonate of potassium and hydrogen" ($KHCO_3$); it is intermediate between carbonate of potassium (K_2CO_3) and carbonate of hydrogen, or true carbonic acid (H_2CO_3); it is "acid carbonate of potassium" or "hydrogen potassium carbonate." Hence in constitution it is an acid salt, although not acid to the taste.

Salts whose specific names end in the syllable "*ate*" (carbon*ate*, sulph*ate*, etc.) are in general conventionally so termed when they contain the radical, or the characteristic elements, of an acid whose name ends in "*ic*," and from which acid they have been or may be formed. Thus the syllable "*ate*," in the words sulph*ate*, nitr*ate*, acet*ate*, carbon*ate*, etc., indicates that the respective salts contain the radical of an acid whose name ends in *ic*, the previous syllables sulph-, nitr-, acet-, carbon-, indicating what that acid is—sulphuric, nitric, acetic, or carbonic. Occasionally a letter or syllable is dropped from or added to a word to render the name more euphonious; thus the sulphuric radical forms sulphates, not sulphurates.

Citrate of Potassium.

Fifth Synthetical Reaction.—Dissolve a few grains or more of carbonate of potassium in water, and add citric acid ($H_3C_6H_5O_7$) until it no longer causes effervescence. The resulting liquid is a solution of citrate of potassium ($K_3C_6H_5O_7$). Evaporate to dryness, in an open dish, cautiously so as to avoid charring; a pulverulent or granular residue is obtained, which is the official *Potassii Citras* (B.P.), the old Citrate of Potash, a white deliquescent powder.

$$\underset{\text{Carbonate of potassium.}}{3K_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\text{Citrate of potassium.}}{2K_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

Citrates.—The citric radical or group of elements, which with three atoms of hydrogen forms a molecule of citric acid, and with three of potassium citrate of potassium, is a trivalent grouping; hence the three atoms of potassium in a molecule of the citrate. The full chemistry of citric acid and other citrates will be described subsequently.

Nitrate of Potassium (KNO_3) (*Potassii Nitras*, B.P.), the old Nitrate of Potash, and *Sulphate of Potassium* (K_2SO_4) (*Potassii Sulphas*, B.P.), the old Sulphate of Potash, could obviously also be made by saturating nitric acid (HNO_3) and sulphuric acid (H_2SO_4), respectively, with carbonate of potassium. Practically they are not made in that way,—the nitrate occurring, as already stated, in nature, and the sulphate as a by-product in many operations. Both salts will be alluded to hereafter in connection with nitric acid.

Tartrate of Potassium.

Sixth Synthetical Reaction.—Place a few grains of carbonate of potassium in a test-tube with a little water, heat to the boiling-point, and then add acid tartrate of potassium ($KHC_4H_4O_6$) till there is no more effervescence; a solution of neutral tartrate of potassium ($KKC_4H_4O_6$) results, the *Potassii Tartras* of the British Pharmacopœia, the old Tartrate of Potash or "Soluble Tartar." Crystals (4- or 6-sided prisms) may be obtained on concentrating the solution by evaporation and setting the hot liquid aside. Larger quantities are made in the same way, 20 of acid tartrate and 9 of carbonate (with 50 of water) being about the proportions necessary for neutrality.

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} = \underset{\text{Neutral tartrate of potassium.}}{2K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Tartrates.—$C_4H_4O_6$ are the elements characteristic of all tartrates: they form a bivalent grouping; hence the formula of the hydrogen tartrate, or tartaric acid, is $H_2C_4H_4O_6$; that of the potassium tartrate $K_2C_4H_4O_6$; of the intermediate salt, the acid potassium tartrate (cream of tartar), $KHC_4H_4O_6$. If the acid tartrate of one metal and the carbonate of another react, a neutral dimetallic tartrate results, as seen in Rochelle Salt ($KNaC_4H_4O_6$), the *Soda Tartarata* of the British Pharmacopœia.

Acid salts (*e.g.* $KHC_4H_4O_6$), that is, salts intermediate in composition between a neutral salt (*e.g.* $K_2C_4H_4O_6$) and an acid (*e.g.* $H_2C_4H_4O_6$), will frequently be met with. All acidulous radicals, except those which are univalent, may be concerned in the formation of such acid salts.

Iodide of Potassium.

Seventh Synthetical Reaction.—Into solution of potash, heated in a test-tube, flask, or evaporating-basin, according to quantity, stir a little solid iodine. The deep colour of the iodine disappears entirely. This is due to the formation of the colourless salts, iodide of potassium (KI) and iodate of potassium (KIO_3), which remain dissolved in the liquid. Continue the addition of iodine so long as its colour, after a few minutes' warming and stirring, disappears. When the whole of the potash in the solution of potash has been converted into the salts mentioned, the slight excess of iodine remaining in the liquid will colour it, and thus show that this stage of the operation is completed.

$$\underset{\text{Hydrate of potassium.}}{6KHO} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Iodide of potassium.}}{5KI} + \underset{\text{Iodate of potassium.}}{KIO_3} + \underset{\text{Water.}}{3H_2O}$$

Separation of the iodide from the iodate.—Evaporate the solution to dryness. If each salt were required, the resulting mixture might be digested in spirit of wine, which dissolves the iodide, but not the iodate. But the iodide only is needed. Intimately mix the residue, therefore (reserving a grain or two for a subsequent experiment), with excess (about a third of its weight) of charcoal, and gently heat in in a test-tube or crucible until slight deflagration ensues.* The crucible may be held in a spirit or air-gas flame, or other fire, by tongs. (Scissors-shaped and other "crucible-tongs" are sold by all makers of apparatus.) The iodide remains unaffected; but the iodate loses all its oxygen, and is thus also reduced to the state of iodide.

$$\underset{\substack{\text{Iodate of}\\\text{potassium}}}{2KIO_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\substack{\text{Iodide of}\\\text{potassium.}}}{2KI} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{6CO}$$

Treat the mass with a little water, and filter to separate excess of charcoal; a solution of pure iodide of potassium results. The latter may be used as a reagent or it may be evaporated to a small bulk and set aside to crystallize.

This is the official process (*Potassii Iodidum*, B.P.).

Properties.—Iodide of potassium crystallizes in small cubical crystals, very soluble in water, less so in spirit. One part in ten of water forms "Solution of Iodide of Potassium," B.P. Exposed to air and sunlight, pure iodide of potassium becomes slightly brown, owing to the liberation of iodine. Under these circumstances a little carbonate of potassium is produced by action of the atmospheric carbonic acid, hydriodic acid (HI) is set free, and the latter, attacked by oxygen, yields a trace of water and of free iodine.

The addition of charcoal in the above process is simply to facilitate the removal of the oxygen of the iodate of potassium. Iodate of potassium (KIO_3) is analogous in constitution, and in composition, so far as the atoms of oxygen are concerned, to chlorate of potassium ($KClO_3$), which has already been stated to be more useful than any other salt for the actual preparation of oxygen gas itself. Hence the removal of the oxygen of the iodate might be accomplished by heating the residue without charcoal. In that case the liberated oxygen would be detected on inserting the incandescent extremity of a strip of wood into the mouth of the test-tube in which the mixture of iodide and iodate had been heated. The charcoal, however, burns out the oxygen more quickly, and thus economizes both heat and time.

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* If, in the operation of heating iodate of potassium with charcoal, excess of the latter be employed, slight incandescence rather than deflagration occurs; if the charcoal be largely in excess, the reduction of the iodate to iodide of potassium is effected without visible deflagration or even incandescence.

Deflagration means violent burning, from *flagratus*, burnt (*flagro*, to burn), and *de*, a prefix augmenting the sense of the word to which it may be attached. Paper thrown into a fire simply burns, nitre deflagrates. *De*tonate (*detono*) is a precisely similar word, meaning to explode with violent noise.

Note.—The formula of iodide of potassium (KI) shows that the salt contains potassium and iodine in atomic proportions. A reference to the table of atomic weights at the end of the volume, and a rule-of-three sum, would therefore show what weight of salt is producible from any given weight of iodine.

Detection of iodate in iodide of potassium.—Iodate of potassium remaining as an impurity in iodide of potassium may be detected by adding to a solution of the latter salt some weak acid (say, tartaric), shaking, and then adding mucilage of starch; blue "iodide of starch" is formed if a trace of iodate be present, but not otherwise. By the reaction of the added acid and the iodate of potassium, iodic acid (HIO_3) is produced; and by reaction of the added acid and the iodide of potassium, hydriodic acid (HI) is produced; neither of these alone attacks starch, but by reaction on each other they give free iodine, which then forms the blue colour. This experiment should be tried on a grain or two of pure iodide and on the impure iodide reserved from the previous experiment. Iodide of potassium containing iodate would obviously yield free iodine, which is excessively corrosive, on the salts coming into contact with the acids of the stomach. $HIO_3 + 5HI = 3H_2O + 3I_2$.

Note on Nomenclature.—The syllable *ide* attached to the syllable *iod* in the name "iodide of potassium," indicates that the *element* iodine is combined with the potassium. An iod*ate*, as already explained, is a salt containing the characteristic elements of iod*ic* acid and of all iodic compounds.

Inorganic salts, one of whose names ends in *ide*, are those which are, or may be, formed from *elements*. The names of salts which are, or may be, formed from compounds include other syllables, *ate* being one (*see* page 75). The only other syllable is *ite*, which is included in the names of salts which are, or may be, formed from the acids and radicals whose names end in *ous*: thus sulph*ite* of sodium, etc. To recapitulate:—An inorganic salt whose name ends in *ate* contains a compound acidulous radical whose name ends in *ic*; a salt whose name ends in *ite* contains a compound acidulous radical whose name ends in *ous*; an inorganic salt whose name ends in *ide* contains an element for its acidulous radical. Thus sulph*ide* relates to sulphur, sulph*ite* to the sulphurous radical, sulph*ate* to the sulphuric radical, and so on with other inorganic "ides," "ites," or "ates."

Bromide of Potassium (*Potassii Bromidum*, B.P.).—This salt is identical in constitution with iodide of potassium, and is made in exactly the same way, bromine being substituted for iodine. The formula of bromic acid is $HBrO_3$. It will be noticed that the following equations are similar in character to those showing the preparation of iodide of potassium:—

$$\underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{6KHO} + \underset{\text{Bromine.}}{3Br_2} = \underset{\substack{\text{Bromide of}\\\text{potassium.}}}{5KBr} + \underset{\substack{\text{Bromate of}\\\text{potassium.}}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\substack{\text{Bromate of}\\\text{potassium.}}}{2KBrO_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\substack{\text{Bromide of}\\\text{potassium.}}}{2KBr} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{6CO} \quad .$$

Manganates of Potassium.

Eighth Synthetical Reaction.—Place a fragment of solid caustic potash (KHO), with about the same quantity of chlorate of potassium ($KClO_3$) and of black oxide of manganese (MnO_2), on a piece of platinum foil.* Hold the foil, by a small pair of forceps or tongs, in the flame of a blowpipe for a few minutes until the fused mixture has become dark-green—apparently black. This colour is that of *manganate of potassium* (K_2MnO_4).

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* The foil may be 1 in. broad by 2 in. long. No ordinary flame will melt the platinum, fused caustic alkalies only slowly corrode it, and very few other chemical substances affect it at all; hence the same piece may be used in experiments over and over again. Most metals form a fusible alloy with platinum, and phosphorus rapidly attacks it; hence such substances, as well as mixtures likely to yield them, should be heated in a small porcelain crucible.

$$\underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{6KHO} + \underset{\substack{\text{Chlorate of}\\\text{potassium.}}}{KClO_3} + \underset{\substack{\text{Black oxide of}\\\text{manganese.}}}{3MnO_2} = \underset{\substack{\text{Manganate of}\\\text{potassium.}}}{3K_2MnO_4} + \underset{\substack{\text{Chloride of}\\\text{potassium.}}}{KCl} + \underset{\text{Water.}}{3H_2O}$$

Ninth Synthetical Reaction.—Permanganate of Potassium ($K_2Mn_2O_8$) (*Potassii Permanganas*, B.P.), the old Permanganate of Potash, which is purple, is obtained, or rather a solution of it, on placing the foil and its adherent mass in water, and boiling for a short time.

$$\underset{\substack{\text{Manganate of}\\\text{potassium.}}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Permanganate}\\\text{of potassium.}}}{K_2Mn_2O_8} + \underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{4KHO} + \underset{\substack{\text{Black oxide}\\\text{of manganese.}}}{MnO_2}$$

On the large scale, the potash set free in the reaction is neutralized by sulphuric or, better, carbonic acid, and the solution evaporated to the crystallizing point. Further details will be given in connection with manganese.

Solutions of (green) manganate or (purple) permanganate of potassium and of sodium so readily yield their oxygen to organic matter, that they are used on the large scale as disinfectants.

Synthetical Reactions, bringing under consideration the remaining official compounds (namely, bichromate, arsenite, chlorate, cyanide, ferrocyanide, and ferricyanide of potassium), are deferred at present.

Crystallization.—This operation will have been performed several times in the course of the foregoing synthetical experiments. Obviously it offers a mode of separating soluble crystallizable substances from soluble *amorphous* (*a*, without; *μορφὴ*, *morphe*, shape) substances; also of separating from each other substances of varying degrees of solubility, or which crystallize with varying degrees of readiness—*fractional crystallization.*

(*b*) *Reactions having Analytical Interest* (*Tests*).

Note.—These are reactions utilized in searching for small quantities of a substance (in the present instance potassium) in a solution. They are best performed in test-tubes or other small vessels. Each reaction should be expressed, in the form of an equation or diagram, in the student's note-book. *All previous or future equations given in this volume should be transferred to the note-book in the form of diagrams, constructed as described on pages* 64 to 67, unless the student can with ease construct equations without the aid of the Manual.

*First Analytical Reaction.**—To a solution of any salt of potassium (chloride,† for example) add a few drops of hydrochloric acid and of a solution of perchloride of platinum ‡ ($Pt\,Cl_4$), and stir the mixture with a glass rod; a yellow granular or slightly crystalline precipitate § slowly forms. (This precipitate is the double chloride of platinum and potassium, and its composition is expressed by the formula $PtCl_4, 2KCl$.)

Memoranda.—When the precipitate is long in forming, it is sometimes of an orange-yellow tint. If iodide of potassium happen to be the potassium salt under examination, some iodide of platinum (PtI_4) will also be formed, giving a red colour to the solution, and a larger quantity of the *precipitant* (that is, the precipitating agent) will be required.

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* As already indicated, chemical reactions are scarcely analytical or synthetical in themselves, but, rather, performed with an analytical or synthetical object. Indeed, not infrequently one and the same reaction is both a synthetical and an analytical reaction. Thus this first, so-called, "analytical reaction" is a synthetical reaction if performed with the object of preparing a specimen of the double chloride of platinum and potassium. It is an analytical reaction, or, rather, has analytical interest, if performed with the object of demonstrating the presence of potassium. Chemical reactions in themselves are operations, not so much of analysis (resolution) or synthesis (combination), or of analysis and synthesis conjoined, as of what has sometimes been termed *metathesis* (transposition). Molecules are not torn to atoms in an operation performed with an analytical object, nor are the atoms put together or set together in an operation (perhaps the same operation) performed with a synthetical object; but in both operations the atoms of the molecules undergo metathesis, that is, exchange places, or are transposed. In short, chemists use the words "analytical" and "synthetical" in a conventional rather than a strictly etymological sense.

† A few fragments of carbonate of potassium, two or three drops of hydrochloric acid, and a small quantity of water, give a solution of chloride of potassium at once, $K_2CO_3 + 2HCl = 2KCl + H_2O + CO_2$.

‡ Experiments with such expensive reagents as perchloride of platinum are economically performed in watch-glasses, drops of the liquids being operated on.

§ By *precipitation* (from *præcipitare*, to throw down suddenly) is simply meant the formation of particles of solid in a liquid, no matter whether the solid, the *precipitate*, subsides or floats, and no matter whether the operation be entire and complete or partial and fractional.

Precaution.—Only chloride of potassium forms this characteristic compound: hence, if the potassium salt in the solution is known not to be a chloride, or if its composition is unknown, a few drops of hydrochloric acid must be added, otherwise some of the perchloride of platinum will be utilized for its chlorine only, the platinum being wasted. Thus, if nitrate of potassium (KNO_3) be the salt present, a little hydrochloric acid enables the potassium to assume the form of chloride when the perchloride of platinum is added, nitric acid (HNO_3) being set free.

Explanation.—The precipitate is, practically, insoluble in water. It is for this reason that a very small quantity of any soluble potassium salt (or, rather, of the potassium in that salt) is thrown out of solution by perchloride of platinum.

Note on Nomenclature.—When distinct molecules of salts unite and form a single crystalline compound, the product is often termed a *double* salt. The double chloride of potassium and platinum is such a body.

Educational Note.—The thoughtful student will not confuse *the test* with the *chemistry of the test.* The test itself appeals to the senses; commonly to the eye, sometimes to the nose, occasionally to the ear. A person may be able to apply a test, and yet never know anything of the chemistry of a test.

Acid Tartrate of Potassium.

Second Analytical Reaction.—To a solution of any salt of potassium add excess of strong solution of tartaric acid ($H_2C_4H_4O_6$), and shake or well stir the mixture; a white granular precipitate (acid tartrate of potassium, $KHC_4H_4O_6$) will be formed.

Note.—By "excess" of any test-liquid (such as the "solution of tartaric acid" just mentioned) is meant such a quantity as is *probably* rather more than sufficient to convert the whole weight of the compound attacked into the compound produced. Thus, in the present case, enough acid must be added to convert the whole of the potassium salt operated on into acid tartrate of potassium. What the weight of salt operated on was must be mentally estimated, roughly, by the operator. It is not necessary in analysing to know the exact weights of salts employed. The analyst must use his judgment, founded on his knowledge of the reaction (as shown by an equation), and of the molecular weights of the substances employed in the reaction, as well as by the rough estimate of the amount of material on which he is experimenting.

Limits of the Test.—Acid tartrate of potassium is soluble in about 180 parts of cold and in 6 parts of boiling water. Hence, in applying the tartaric test for potassium, the solutions must not be hot. Even if cold, no precipitate will be obtained if the solutions are very dilute. This test, therefore, is of far less value than that first mentioned. The acid tartrate of potassium is less soluble in diluted alcohol than in water, so that the addition of spirit of wine renders the reaction somewhat more delicate.

Cream of Tartar.—The precipitate is the *Potassii Tartras Acida* of the British Pharmacopœia, the old Acid Tartrate or Bitartrate of Potash or Cream of Tartar, though the official preparation is not formed in the above manner; on the contrary, the acid is derived from the salt, which, often mixed with some tartrate of calcium, occurs naturally in the juice of many plants.

Third Analytical Reaction.—The *flame*-test. Dip the looped end of a platinum wire into a solution containing a potassium salt, and introduce the loop into the lower part of a spirit-flame, the flame of a mixture of gas and air, a blowpipe-flame, or other slightly coloured flame. A light violet or lavender tint will be communicated to the flame, an effect highly characteristic of salts of potassium.

Fourth Analytical Fact.—Salts of potassium are not readily volatile. Place a fragment of carbonate, nitrate, or other potassium salt, on a piece of platinum foil, and heat the latter in the flame of a lamp; the salt may fuse to a transparent liquid and flow over the foil; water also, if present, will escape as steam, and black carbon be set free if the salt happen to be a tartrate, citrate, etc.; but the potassium compound itself will not be vaporized. This is a valuable negative property, as will be evident when the analytical reactions of ammonium come under notice.

QUESTIONS AND EXERCISES.

Name the sources of potassium.—Give the source, formula, and characters of Carbonate of Potassium.—Distinguish between synthetical and analytical reactions.—How is the official *Liquor Potassæ* prepared?—What is the systematic name of Caustic Potash?—State the chemical formula of Caustic Potash.—Construct an equation or diagram expressive of the reaction between carbonate of potassium and slaked lime.—Define a *hydrate*.—What group of atoms is characteristic of all carbonates?—Define the term *radical*.—How is "Sulphurated Potash" made, and of what salts is it a mixture?—What is the formula of the radical of all acetates?—Draw a diagram showing the formation of Acetate of Potassium.—Give a process for the conversion of carbonates into other salts.—What is the difference between Carbonate and Bicarbonate of Potassium? How is the latter prepared?—What is the relation between salts whose specific names end in the syllable "*ate*," and acids ending in "*ic*"?—Draw out diagrams or equations descriptive of the formation of Tartrate of Potassium from the Acid Tartrate, and Citrate from the Carbonate of Potassium.—Distinguish between a neutral and an acid salt.—How is Iodide of Potassium made?—Illustrate the process either by diagrams or equations.—Work out a sum showing how much iodide of potassium is producible from 1,000 grains of iodine. *Ans.*, 1,307 grains.—Give a method for the detection of iodate in iodide of potassium.—Explain the reaction.—Has the syllable "*ide*" any general signification in chemical nomenclature?—State the relations between sulphides, sulphites, and sulphates.—Mention the chemical relation of Bromide to Iodide of Potassium.—Describe the formation of Permanganate of Potassium, giving equations or diagrams.—How do manganates and permanganates act as disinfectants?—Enumerate the tests for potassium, explaining by diagrams or equations the various reactions which occur.

SODIUM.

Symbol, Na. Atomic weight, 23.
Formula, Na_2. Probable molecular weight, 46.

Memoranda.—Most of the sodium salts met with in pharmacy are obtained directly from carbonate of sodium, which is now manufactured on an enormous scale from chloride of sodium (common salt, sea-salt, bay-salt, or rock-salt), the natural source of the sodium salts. When pure, salt (*Sodii*

Chloridum, B.P.) occurs "in small white crystalline grains, or transparent cubic crystals, free from moisture;" the best varieties commonly contain a little chloride of magnesium, and sometimes other impurities. Besides the direct and indirect use of carbonate of sodium, or carbonate of soda, as it is commonly called, in medicine, it is largely used for household cleansing purposes, under the name of "soda," and in the manufacture of soap. Nitrate of sodium also occurs in nature, but is valuable for its nitric constituents rather than its sodium. Sodium is a constituent of about forty chemical or galenical preparations of the British Pharmacopœia.

Sodium (*Sodium*, B.P.) is prepared by a process similar to that for potassium, but with less difficulty. Castner obtains it comparatively cheaply by distillation from a mixture of soda, carbon, and iron, contained in steel vessels. It has a bright metallic lustre when freshly cut, but rapidly absorbs oxygen and carbonic acid gas from the air, and thus becomes coated with carbonate of sodium. It displaces hydrogen from water, yielding solution of hydrate of sodium; but unless the sodium is confined to one spot, by placing it on a small floating piece of filter-paper, the action is not sufficiently intense to cause ignition of the escaping hydrogen. When the latter does ignite, it burns with a yellow flame, due to the presence of a little vapour of sodium.

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrogen.}}{H_2} + \underset{\text{Hydrate of sodium.}}{2NaHO.}$$

It similarly attacks alcohol, yielding "ethylate of sodium" (*see* Index). It may be kept beneath the surface of a liquid containing neither moisture nor oxygen (mineral naphtha). It crystallizes in octahedra. Its atom is univalent, Na'.

REACTIONS HAVING (*a*) SYNTHETICAL AND (*b*) ANALYTICAL INTEREST.

(*a*) *Reactions having Synthetical Interest.*

Hydrate of Sodium. Caustic Soda.

First Synthetical Reaction.—The formation of solution of hydrate of sodium or caustic soda, NaHO (*Liquor Sodæ*, B.P.), the old Hydrate of Soda. This operation resembles that of making solution of potash, already described.

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Hydrate of sodium.}}{2NaHO} + \underset{\text{Carbonate of calcium.}}{CaCO_3}.$$

The practical student should apply to this solution the remarks made concerning solution of potash.

The official *Liquor Sodæ* is made from 28 ounces of crystals of carbonate of sodium, 12 of washed slaked lime, and 1 gallon of water, under precisely similar circumstances to those detailed for *Liquor Potassæ* (p. 64). If the solution be evaporated to dryness, and the residue fused and poured into moulds, solid hydrate of sodium (*Soda Caustica*, B.P.) is obtained. Caustic soda is largely employed in various manufactures.

Second Synthetical Reaction.—The reaction of sulphur and carbonate of sodium at a high temperature resembles that of sulphur and carbonate of potassium; but as the product is not used in medicine the experiment may be omitted. It is mentioned here to draw attention to the close resemblance of the potassium salts to those of sodium.

Acetate of Sodium.

Third Synthetical Reaction.—Add carbonate of sodium (in powder or, better, in fragments) to some strong acetic acid in an evaporating-basin as long as effervescence occurs, and then boil off some of the water.* When the fluid is cold, crystals of Acetate of Sodium, B.P. ($NaC_2H_3O_2$, $3H_2O$), the old Acetate of Soda (*Sodii Acetas*, U.S.P.) will be deposited. A ten per cent. solution in distilled water forms the " Solution of Acetate of Sodium," B.P.

$$\underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of sodium.}}{2NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}.$$

Acetate of sodium effloresces in dry air, and loses all its water of crystallization when gently heated. It supports a temperature of 270° F. or 280° without decomposition, but above 300° soon chars.

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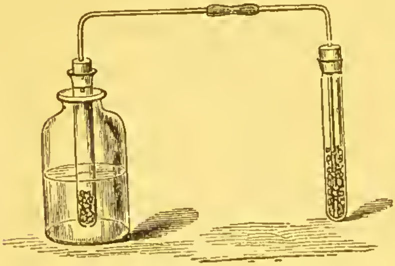
* The " water " alluded to occurs in the acid, which, though commonly termed " acetic acid," is really a solution of that acid in water.

Bicarbonate of Sodium.

Fourth Synthetical Reaction.—The action of carbonic acid (H_2CO_3), or carbonic acid gas (CO_2) and water (H_2O), on carbonate of sodium (Na_2CO_3) resembles that on carbonate of potassium, but is applied in a different manner. The result is Bicarbonate of Sodium ($NaHCO_3$) (*Sodii Bicarbonas*, B.P.), the old Bicarbonate of Soda.

$$\begin{array}{ccccccc} Na_2CO_3 & + & H_2O & + & CO_2 & = & 2NaHCO_3. \\ \text{Carbonate} & & \text{Water.} & & \text{Carbonic} & & \text{Bicarbonate} \\ \text{of sodium.} & & & & \text{acid gas.} & & \text{of sodium.} \end{array}$$

Fig. 17.



PREPARATION OF BICARBONATE OF SODIUM.

Process.—Heat crystals of carbonate of sodium in a porcelain crucible until no more steam escapes. Rub the product, in a mortar, with two-thirds its weight of more of the crystals, and place the powder in a test-tube or small bottle into which carbonic acid gas may be conveyed by a tube passing through a cork and terminating at the bottom of the vessel. To generate the carbonic acid gas, fill a test-tube having a small hole in the bottom (or a similar piece of glass tubing, of which one end is plugged by a grooved cork) with fragments of marble, insert a cork and delivery-tube, and connect the latter with the similar tube of the vessel containing the carbonate of sodium by a piece of india-rubber tubing. Now plunge the tube of marble into a test-glass, or other vessel, containing a mixture of one part hydrochloric acid and two parts water, and loosen the cork of the carbonate-of-sodium tube until carbonic acid gas, generated in the marble tube, may be considered to fill the whole arrangement; then replace the cork tightly and set the apparatus aside. As the gas is absorbed by the carbonate of sodium, hydrochloric acid rises into the marble tube and generates fresh gas, which, in its turn, drives back the acid liquid, and thus prevents the production of any more gas until further absorption has occurred. When the salt is wholly converted into bicarbonate ($NaHCO_3$), it will be found to have become damp through the liberation of water from the crystallized carbonate (Na_2CO_3, $10H_2O$). (It would be inconveniently moist, even semi-fluid, if a part of the carbonate had not previously been rendered anhydrous.) On the large scale the resulting bicarbonate may be freed from any carbonate or traces of other salts, by adding half its bulk of cold distilled water, setting aside for about half an hour, shaking occasionally, draining the undissolved portion, and drying it by exposure on filtering paper.

This arrangement of apparatus for *Sodii Bicarbonas*, B.P., may be adopted for *Potassii Bicarbonas*, B.P., one part of carbonate dissolved in two and a half parts of water being subjected to the action of the gas, and not the solid carbonate, as in the case of the sodium salt.

The carbonate of sodium may be placed, not in a test-tube or bottle, but in a vertical tube, the bottom of which is loosely closed by a grooved cork. Any water of crystallization that is set free then runs off (into a basin or cup beneath), and takes with it impurities (chlorides or sulphates, etc.) that may have been present in the original salt.

Sodium Carbonates by "The Ammonia Process."

Bicarbonate of sodium is prepared by bringing to the elements of bicarbonate of ammonium a strong solution of common salt; the bicarbonate of sodium is precipitated.

$$\underset{\substack{\text{Bicarbonate}\\\text{of ammonium.}}}{NH_4HCO_3} + \underset{\substack{\text{Chloride}\\\text{of sodium.}}}{NaCl} = \underset{\substack{\text{Bicarbonate}\\\text{of sodium.}}}{NaHCO_3} + \underset{\substack{\text{Chloride of}\\\text{ammonium.}}}{NH_4Cl.}$$

The resulting chloride of ammonium is reconverted into carbonate (p. 100), the latter more fully carbonated, and again used for producing bicarbonate of sodium. Carbonate of Sodium (*Sodii Carbonas*, B.P.) is made by heating the bicarbonate thus obtained, the carbonic acid then liberated serving for the conversion of some carbonate of ammonium into bicarbonate of ammonium.

$$\underset{\text{Bicarbonate of sodium.}}{2NaHCO_3} = \underset{\text{Carbonate of sodium.}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

A *crystal* of carbonate of sodium is carbonate of sodium plus water; on heating it, more or less of the water is evolved, and *anhydrous* carbonate of sodium is partially or wholly produced (*Sodii Carbonas Exsiccata*, B.P.).

$$\underset{\text{Crystallized carbonate of sodium (286).}}{Na_2CO_3, 10H_2O} - \underset{\text{Water (180).}}{10H_2O} = \underset{\text{Dried carbonate of sodium (106).}}{Na_2CO_3}$$

Note on Nomenclature.—Anhydrous bodies (from α, and ὕδωρ, *hudōr*, *i.e.* without water) are compounds from which water has been taken, but whose essential chemical properties are unaltered. Salts containing water are *hydrous* bodies; of these the larger portion are crystalline, and their water is then termed *water of crystallization.* Non-crystalline *hydrous* compounds were formerly spoken of as *hydrated* substances; hydrates are, however, a distinct class of bodies, salts derived from water by one-half of its hydrogen becoming displaced by an equivalent quantity of another radical. *Anhydrides* form still another distinct class of chemical substances; they are derived from acids: in short, they are acids from which, not exactly water as water, but the elements of water, have been removed, the essential chemical (acid) properties being thereby greatly altered. (For illustrations, *see* Index, "Anhydrides.")

Water of Crystallization.—The water in crystallized carbonate of sodium is in the solid condition, and, like ice and other fusible substances, requires heat for its liquefaction. Many salts (freezing mixtures) when dissolved in water give a very cold solution. This is because they and their solid water, if they have any, are then, absorbing some heat from surrounding media, converted into liquids. Take away from water some of its heat, the result is ice. Give to ice (at 32° F.) more heat than it contains already, the result is water (still at 32° F.). (Heat thus taken into a substance without increasing its temperature is said to become *latent*—from *latens*, hiding; it is no longer discoverable by the sense of touch or the thermometer. The term *latent* gives a somewhat incorrect idea, however, of the conditions; for our knowledge of the extent and readiness with which one form of force is convertible into another renders highly probable the assumption that heat is in these cases converted into motion, the latter enabling the molecules of a solid to take up the new positions demanded by their liquid condition.) The only apparent difference between ice and the water in such crystals as carbonate of sodium, is that ice is solid water in the free, and water of crystallization solid water in the combined state. The former can only exist at and below 32° F., the latter may exist at ordinary temperatures. Salts which unite with little or even no water of crystallization at common temperatures, but take up much at very low temperatures, are termed *cryohydrates* (κρυος, *kruos*, icy cold, frost). All water of crystallization is dispelled at high temperatures. In chemical formulæ, the symbols representing water are usually separated by a comma from those representing salts. The crystals of acetate of sodium (of the third reaction) contain water in this loose state of combination—water of crystallization ($NaC_2H_3O_2, 3H_2O$). It is possible, however, that this so-called water of crystallization is in a more intimate state of combination than is indicated by such a formula as that just given.

"*Soda-water.*"—A solution of bicarbonate of sodium in water charged with carbonic acid gas under pressure constitutes the official *Liquor Sodæ Effervescens*, B.P., and like the official "potash-water" is a true *medicine*, an antacid. The ordinary *beverage* "soda-water" is commonly a simple solution of carbonic acid gas in water, and would be more appropriately termed "aërated water": any medicinal effect it may possess is due to the sedative influence of its carbonic acid gas on the coats of the stomach. Originally it contained a little "soda," and was a mild antacid, but the public took to it as a mere beverage, refusing to drink it if it contained any "soda," yet persisted, and still persist, in calling it "soda-water." At common temperatures water dissolves about its own volume of carbonic acid gas, both being under the same pressure. One pint of the official soda-water contains 30 grains of bicarbonate of sodium and a pint of carbonic acid gas; but the solution is under a pressure of four atmospheres, in addition to the ordinary pressure of our atmosphere, five atmospheres altogether, so that five pints of the gas at ordinary atmospheric pressure are required for the quantity mentioned.

Solubility of gases in water.—Whatever the weight and volume of a gas dissolved by a liquid at ordinary atmospheric pressure, that weight is doubled by double pressure, the two original volumes of gas thereby being reduced to one; trebled at treble pressure, the three original volumes of gas being reduced to one; quadrupled at quadruple pressure, the four original volumes of gas being reduced to one, and so on. This is a general law (Henry and Dalton) regarding the solubility of gases in liquids under given temperatures. An average bottle of "soda-water" contains about five times the weight of carbonic acid gas which can exist in it without artificial pressure; so that on removing its cork four times its bulk escapes, its own bulk remaining dissolved.

Note.—Bicarbonate of sodium may also be medicinally administered in the form of lozenge (*Trochisci Sodii Bicarbonatis*, B.P.).

Tartrate of Potassium and Sodium.

Fifth Synthetical Reaction.—To some hot strong solution of carbonate of sodium (about three parts), in a test-tube or larger vessel, add acid tartrate of potassium (about four parts) till no more effervescence occurs; when the solution is cold, crystals of the tartrate of potassium and sodium (*Soda Tartarata*, B.P., *Potassii et Sodii Tartras*, U.S.P.), the old *Rochelle Salt* or Tartrate of Potash and Soda, will be deposited ($KNaC_4H_4O_6, 4H_2O$). The crystals are usually halves of right rhombic prisms.

$$\underset{\substack{\text{Carbonate}\\\text{of sodium.}}}{Na_2CO_3} + \underset{\substack{\text{Acid tartrate}\\\text{of potassium.}}}{2KHC_4H_4O_6} = \underset{\substack{\text{Tartrate of potassium}\\\text{and sodium.}}}{2KNaC_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid-gas.}}}{CO_2}$$

Tartaric acid	$HH\ C_4H_4O_6$
Acid tartrate of potassium . . .	$KH\ C_4H_4O_6$
Tartrate of potassium and sodium .	$KNaC_4H_4O_6$

Very close analogy will be noticed in the above formulæ indicative of the analogy in the constitution of the molecules of these salts. When the other tartrates come under notice, it will be found that they also have a similar constitution.

Hypochlorite of Sodium.

Sixth Synthetical Reaction.—Triturate in a mortar 2 parts of chlorinated lime with a solution of 3 of carbonate of sodium in 20 of water. Filter. The product is the official solution of chlorinated soda (*Liquor Sodæ Chlorinatæ*, B.P.).

$$\underset{\text{Chlorinated lime.}}{CaCl_2O_2CaCl_2} + \underset{\text{Carbonate of sodium.}}{2Na_2CO_3} = \underset{\text{Chlorinated soda.}}{(NaClO,NaCl)_2} + \underset{\text{Carbonate of calcium.}}{2CaCO_3}$$

This solution is an old and very useful disinfectant, formerly known as *Labarraque's* liquor and *Eau de Javelle.* It contains about 2½ per cent. of available chlorine.

Iodide and Bromide of Sodium.

These salts (NaI and NaBr), *Sodii Iodidum*, B.P., and *Sodii Bromidum*, B.P., are similar to the iodide and bromide of potassium in constitution, and are prepared with the same manipulations, soda being used in place of potash. The bromide of sodium, however, must be crystallized from warm solutions, or rhombic prisms containing water ($NaBr, 2H_2O$) will be deposited.

Other Sodium Compounds.

Synthetical Reactions portraying the chemistry of the remaining official compounds (namely, nitrate, sulphate, hyposulphite, borate, arseniate, valerianate and ethylate of sodium) are deferred until the several acidulous radicals of these salts have been described.

Phosphate of Sodium.—The preparation and composition of this salt will be most usefully studied after bone-ash, the source of it and other phosphates, has been described. Bone-ash is phosphate of calcium. (*See* page 123.)

The official Citro-Tartrate of Sodium (*Sodii Citro-tartras Effervescens*, B.P.), the old Citro-tartrate of Soda, is a mixture of bicarbonate of sodium (17 parts), citric acid (6), tartaric acid (9), and sugar (5), mixed and heated (to 200° F. or 220°) until the particles aggregate to a granular condition. When required for medicinal use, a dose of the mixture is placed in water; escape of carbonic acid gas at once occurs, and an effervescing liquid results. This substance may be regarded as the official representative of the popular "Effervescing Citrate of Magnesia," so-called, which will be further noticed in connection with the salts of magnesium (page 133).

"*Lemon and Kali*" is a pulverulent mixture of bicarbonate of sodium, tartaric acid, sugar and essence of lemon. It was invented and so named by one Charles Gomond Cooke, who long retained a trade monopoly in the article by thus hiding the "soda" under its ancient name of "kali" (see p. 25), heightening the mystery by the prefix "Lemon and."

Sodii Phosphas Effervescens, B.P., and *Sodii Sulphas Effervescens*, B.P., are the respective *anhydrous* salts mixed with bicarbonate of sodium and tartaric and citric acids.

Soda Powders (*Pulvis Effervescens Compositus*, U.S.P.) are formed of 30 grains of bicarbonate of sodium and 25 of tartaric acid, wrapped separately in papers of different colours. When mixed with water, carbonic acid gas escapes, and tartrate of sodium ($Na_2C_4H_4O_6$) results, a little bicarbonate also remaining.

In the manufacture of Carbonate of Sodium, the old Carbonate of Soda, the source of the sodium is chloride of sodium, and of the carbonic radical carbonate of calcium in the form of limestone. By "the Le Blanc process" the chloride is converted into sulphate, the sulphate then roasted with coal and limestone, and the resulting *black ash* lixiviated. (*Lixivia*, from *lix*, lye—water impregnated with alkaline salts; hence *lixiviation*, the operation of washing a mixture with a view of dissolving out salts.) If relatively small quantities of solvents be employed, the solution by lixiviation will be more or less *fractional*, salts of varying solubility being thus more or less separated from each other. The lye, evaporated to dryness, yields crude carbonate of sodium (soda-ash). By "the ammonia process" the carbonate of sodium is obtained by heating bicarbonate of sodium, the latter by mixing strong solutions of chloride of sodium and bicarbonate of ammonium. The last-named salt results from the action of carbonic acid gas (liberated on heating the bicarbonate of sodium) on carbonate of ammonium, and this again from chloride of ammonium and limestone. By either process common salt and limestone are the ordinary prime sources respectively of the sodium and the carbonic radical in carbonate of sodium. The processes will be further described in connection with Carbonates.

Deliquescence and Efflorescence.—The carbonates of sodium and potassium, chemically closely allied, differ physically. Carbonate of potassium quickly absorbs moisture from the air and becomes damp, wet, and finally fluid—it is *deliquescent* (*deliquescens*, melting away). Carbonate of sodium, on the other hand, yields water of crystallization to the air, the crystals becoming white, opaque, and pulverulent—it is *efflorescent* (*efflorescens*, blossoming forth, in allusion to the appearance of the product).

Analogy of Sodium salts to Potassium salts.—Other synthetical reactions might be described similar to those given under potassium, and thus citrate, iodate, bromate, chlorate, manganate, and permanganate of sodium, and many other salts be formed. But enough has been stated to show how chemically analogous sodium is to potassium. Such analogies will constantly present themselves. In few departments of knowledge are order and method more perceptible; in few is there as much natural law, as much *science*, as in chemistry.

Substitution of Potassium and Sodium salts for each other.—Sodium salts being cheaper than potassium salts, the former may sometimes be economically substituted. That one is employed rather than the other is often merely a result due to accident or fashion. But it must be borne in mind that in some cases a potassium salt will crystallize more readily than its sodium analogue, or that a sodium salt is stable when the corresponding potassium salt has a tendency to absorb moisture, or one may be more soluble than the other, or the two may have different medicinal effects. For these or similar reasons, a potassium salt has come to be used in medicine or trade instead of the corresponding sodium salt, and *vice versâ*. Whenever the acidulous portion only is to be utilized, the least expensive salt of the class would nearly always be selected.

(*b*) *Reactions having Analytical Interest.*

1. *The chief analytical reaction* for sodium is *the flame-test*. When brought into contact with a flame in the manner described under Potassium (page 84), an intensely yellow colour is communicated to the flame by any salt of sodium. This is highly characteristic—indeed, almost too delicate a

test; for if the point of the wire be touched by the fingers, enough salt (which is contained in the moisture of the hand) adheres to the wire to communicate a very distinct sodium reaction. These statements should be experimentally verified, the chloride, sulphate, or any other salt of sodium being employed.

2. Sodium salts, like those of potassium, are not volatile. Prove this fact by the means described when treating of the effect of heat on potassium salts (p. 84).

QUESTIONS AND EXERCISES.

How is the official Solution of Soda prepared? Give a diagram or equation.—Explain the action of sodium or potassium on water. What colours do these elements respectively communicate to flame?—How much bicarbonate of sodium can be obtained from 2,240 pounds of crystallized carbonate? *Ans.*, 1,316 lbs., nearly.—Acetate of Sodium: give formula, process, and equation.—Give a diagram showing the formation of Bicarbonate of Sodium.—Why is a mixture of dried and undried carbonate of sodium employed in the preparation of the bicarbonate?—State the difference between anhydrous and crystallized carbonate of sodium.—Define the terms *anhydrous*, *hydrous*, *hydrate*, *anhydride*.—What do you understand by *water of crystallization*?—What is the nature of the official "*Liquor Sodæ Effervescens*"?—How many volumes of gas (reckoned as at ordinary atmospheric pressure) are contained in any given volume of the official "soda-water"?—What is the general law regarding the solubility of gases in liquids under pressure?—What is the systematic name of *Soda Tartarata*, B.P.? and how is the salt prepared?—What is the relation of Rochelle salt to cream of tartar and tartaric acid?—Give the mode of preparation of the official Solution of Chlorinated Soda, expressing the process by a diagram.—How is the effervescing Citro-tartrate of Sodium prepared?—Define *deliquescence*, *efflorescence*, and *lixiviation*.—State the relations of potassium salts to those of sodium.—How are sodium salts distinguished from those of potassium?

AMMONIUM.

Formula, NH_4. Combining weight, 18.

Memoranda.—The elements nitrogen and hydrogen, in the proportion of one atom to four (NH_4), are those characteristic of all the compounds about to be studied, just as potassium (K) and sodium (Na) are the characteristic elements of the potassium and sodium compounds. Ammonium is a univalent nucleus, root, or radical, like potassium or sodium; and the ammonium compounds closely resemble those of potassium or sodium. In short, if, for an instant, potassium or sodium be imagined to be compounds, the analogy between these three series of salts is complete. Ammonium is said to have been isolated, by Weyl, as an unstable dark-blue liquid, possessing a metallic lustre.

Source.—The source of nearly all the ammoniacal salts met with in commerce is the ammonia gas (NH_3) obtained in distilling all kinds of coal in the manufacture of ordinary illuminating gas and of coke; being derived, doubtless, from the nitrogen of the plants from which the coal has been produced. It is also a by-product in distilling paraffin oil from shale, and may be washed out of the furnace gases of iron-works. It is possible, however, to produce ammonia from its elements. Thus, coal-dust, air, and vapour of water, all at a red heat, yield, according to Rickman and Thompson, gaseous ammonia. Salt added to the mixture prevents the further combustion of the formed ammonia, and chloride of ammonium sublimes. Nitrogen and hydrogen passed over spongy platinum yield traces of ammonia.

Ammonia.—When this gas (NH_3) comes into contact with the condensed steam (H_2O) in the process of cooling the coal-gas, the resulting "ammoniacal liquor" is believed to contain *hydrate* of ammonium (NH_4HO), the analogue of hydrate of potassium (KHO) or sodium ($NaHO$). The grounds for this belief are the observed analogy of the well-known ammoniacal salts to those of potassium and sodium, the similarity of action of solutions of potash, soda, and ammonia on salts of most metals, and the asserted existence of crystals of an analogous sulphur salt (NH_4HS).

Chloride of Ammonium.—The ammonia of the "ammoniacal liquor" of the gas-works, liberated by heat and the concurrent action of lime on sulphydrate, carbonate, and other salts present, and passed into hydrochloric acid, yields crude *chloride of ammonium* (sal-ammoniac), $NH_3 + HCl = NH_4Cl$; and from this salt, purified, the others used in pharmacy are directly or indirectly made. Chloride of Ammonium (*Ammonii Chloridum*, B.P.) occurs "in colourless inodorous minute crystals, or in translucent fibrous masses, tough, and difficult to powder, soluble in water [1 in 10 is the "Solution of Chloride of Ammonium," B.P.] and in rectified spirit."

Chloride of ammonium generally contains slight traces of oxychloride of iron, tarry matter, and possibly chlorides of compound ammoniums (*vide* "Artificial Alkaloids" in Index).

Sulphate of Ammonium $(NH_4)_2SO_4$, the old Sulphate of Ammonia, results when the ammonia from the "ammoniacal liquor" is neutralized by sulphuric acid. It is largely used as a constituent of artificial manure; and when purified by recrystallization, is employed in pharmacy (*Ammonii Sulphas*, U.S.P.).

Volcanic Ammonia.—A very pure form of ammonia is that met with in volcanic districts, and obtained as a by-product in the manufacture of borax; the crude boracic acid as imported contains 5 to 10 per cent. of ammonium salts, chiefly sulphate, and double sulphates of ammonium with magnesium, sodium, and manganese (*Howard*).

REACTIONS HAVING (*a*) GENERAL, (*b*) SYNTHETICAL, AND (*c*) ANALYTICAL INTEREST.

Ammonium Amalgam (?).

(*a*) *General Reaction.*—To forty or fifty grains of dry mercury in a *dry* test-tube, add one or two small pieces of sodium (freed from adhering naphtha by gentle pressure with a piece of filter-paper), and amalgamate by gently warming the tube. To this amalgam, when cold, add some fragments of chloride of ammonium and a strong solution of the same salt. The sodium amalgam soon begins to swell and rapidly increase in bulk, probably overflowing the tube. The light spongy mass produced is the so-called ammonium amalgam, and the reaction is usually adduced as evidence of the existence of ammonium. The sodium of the amalgam unites with the chlorine of the chloride of ammonium, while the ammonium is supposed to form an amalgam with the mercury. As soon as formed the amalgam gives off hydrogen and ammonia gases; this decomposition is nearly complete after some minutes, and mercury remains.

(*b*) *Reactions having Synthetical Interest.*

Hydrate of Ammonium. Ammonia.

First Synthetical Reaction.—Heat a few grains of sal-ammoniac with about an equal weight of hydrate of calcium (slaked lime) damped with a little water in a test-tube;

ammonia gas is given off, and may be recognised by its well-known odour. It is very soluble in water. Pass a delivery-tube fitted to the charged test-tube, as described for the preparation of oxygen and hydrogen, into a second test-tube, at the bottom of which is a little water; again heat, the end of the delivery-tube being only just beneath the surface of the water (or, possibly, all the water might rush back into the generating-tube, water absorbing ammonia gas with great avidity); solution of ammonia (*Liquor Ammoniæ*, B.P., or *Liquor Ammoniæ Fortior*, B.P.) will thus be formed.

$$\underset{\text{Chloride of ammonium.}}{2NH_4Cl} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Ammonia gas.}}{2NH_3}$$

A molecule of ammonia gas is composed of one atom of nitrogen with three atoms of hydrogen; its formula is NH_3. Two volumes of the gas contain one volume of nitrogen combined with three similar volumes of hydrogen. Its constituents have, therefore, in combining suffered condensation to one-half their normal bulk. Its conversion into hydrate of ammonium may thus be shown:—

$$\underset{\text{Ammonia gas.}}{NH_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hydrate of ammonium (ammonia).}}{NH_4HO}$$

Solutions of Ammonia, prepared by this process on a large scale and in suitable apparatus, are met with in pharmacy—the one (sp. gr. 0·891) containing 32·5 per cent., the other (sp. gr. 0·959) 10 per cent. by weight of ammonia gas, NH_3, or 66·9 and 20·6 of ammonia, NH_4HO (*Liquor Ammoniæ Fortior* and *Liquor Ammoniæ*, B.P. One part, *by measure*, of the former, and two of water form the latter). On the large scale, bottles are so arranged in a series as to condense all the ammonia evolved during the operation (*see* British Pharmacopœia.)

Acetate of Ammonium.

Second Synthetical Reaction.—To acetic acid and water in a test-tube add powdered commercial carbonate (acid carbonate and carbamate) of ammonium until effervescence ceases. Solutions having the specific gravities, respectively, of 1·022 and (five times the strength) 1·073, form the official Solutions of Acetate of Ammonium ($NH_4C_2H_3O_2$) (*Liquor*

Ammonii Acetatis, B.P., and *Liquor Ammonii Acetatis Fortior*, B.P.).

On evaporating and cooling, Acetate of Ammonium (the old Acetate of Ammonia) may be obtained in crystals.

$$\underset{\text{Acid carbonate and carbamate of ammonium.}}{NH_4HCO_3,NH_4NH_2CO_2} + \underset{\text{Acetic acid.}}{3HC_2H_3O_2} = \underset{\text{Acetate of ammonium.}}{3NH_4C_2H_3O_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas}}{2CO_2}$$

Solution of Acetate of Ammonium can, of course, be just as easily made by reaction of acetic acid and solution of ammonia (NH_4HO); but the liquid, owing to absence of dissolved carbonic acid, is too vapid for use in pharmacy.

Carbonates of Ammonium.

Commercial carbonate of ammonium is made by heating a mixture of chalk and sal-ammoniac; chloride of calcium ($CaCl_2$) is produced, ammonia gas (NH_3) and water (H_2O) escape, and the ammoniacal carbonate distils or, rather, sublimes* in cakes (*Ammonii Carbonas*, B.P., the old Carbonate of Ammonia). The best form of apparatus to employ is a retort with a short wide neck and a cool receiver. On the large scale the retort is usually iron, and the receiver earthenware or glass; on the small scale glass vessels are employed. The salt is purified by resublimation at a low temperature—150° F. is said to be sufficient.

The salt, the empirical formula of which is $N_3H_{11}C_2O_5$, is probably a mixture of one molecule (sometimes two) of acid carbonate of ammonium (NH_4HCO_3) and one of a salt termed carbamate of ammonium ($NH_4NH_2CO_2$). The latter belongs to an important class of salts known as *carbamates*, but is the only one of direct interest to the pharmacist. Cold water extracts it from the commercial carbonate of ammonium, leaving the acid carbonate or bicarbonate undissolved if the amount of liquid used be very small. Alcohol extracts the carbamate, leaving the acid carbonate undissolved. In water the carbamate soon changes into the neutral carbonate of ammonium—

$$NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3;$$

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* *Sublimation* (from *sublimis*, high). Vaporization of a solid substance by heat, and its condensation on an upper and cooler part of the vessel or apparatus in which the operation is performed. Substances sublime at different temperatures, hence a mixture of volatile solids may sometimes be separated or fractionated by sublimation.

so that an aqueous solution of commercial carbonate of ammonium contains both acid carbonate and neutral carbonate of ammonium. If to such a solution some ordinary solution of ammonia be added, a solution of the *neutral carbonate of ammonium*, only, is obtained: and this is the common reagent always found on the shelves of the analytical laboratory. Thus, "Solution of Carbonate of Ammonium," B.P., is formed by dissolving half an ounce of the salt in ten ounces of water, to which three-quarters of an ounce of solution of ammonia has been added.

$$NH_4HCO_3 + NH_4HO = (NH_4)_2CO_3 + H_2O.$$

Neutral carbonate of ammonium is the salt formed on adding strong solution of ammonia to the commercial carbonate in preparing a pungent mixture for toilet smelling-bottles; but it is unstable, and on continued exposure to air is reduced to a mass of crystals of bicarbonate.

If carbonate of ammonium contain more than traces of empyreumatic matters (from the gas-liquors), an aqueous solution, with excess of sulphuric acid added, will decolourize a dilute solution of permanganate of potassium at once.

Sal Volatile (*Spiritus Ammoniæ Aromaticus*, B.P.) is a spirituous solution of about $1\frac{1}{4}$ per cent. of ammonia gas (NH_3), nearly $3\frac{1}{2}$ per cent. of neutral carbonate of ammonium, $(NH_4)_2CO_3$, and the oils of nutmeg and lemon. Commercial samples contain salts equivalent to from 1 to nearly 3 per cent. of ammonia gas, the official spirit yielding a total of $2\frac{1}{2}$ per cent. of the gas. Fetid spirit of ammonia (*Spiritus Ammoniæ Fœtidus*, B.P.) is an alcoholic solution of the volatile oil of asafœtida mixed with solution of ammonia.

Nitrate of Ammonium.

Third Synthetical Reaction.—To some diluted nitric acid add carbonate of ammonium, until, after well stirring, a slightly ammoniacal odour remains. The solution contains Nitrate of Ammonium (*Ammonii Nitras*, B.P., the old Nitrate of Ammonia).

$$\underset{\substack{\text{Acid carbonate and carbamate}\\\text{of ammonium.}}}{NH_4HCO_3,NH_4NH_2CO_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{3HNO_3} = \underset{\substack{\text{Nitrate of}\\\text{ammonium.}}}{3NH_4NO_3} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{2CO_2}$$

From a strong hot solution of nitrate of ammonium, crystals may be obtained containing much water (NH_4NO_3, $12H_2O$). On heating these in a dish to about 320°F. the water escapes. The anhydrous salt remaining (NH_4NO_3) may be poured on to an iron plate. On further heating the crushed nitrate, at 350° to 450° F., it is resolved into *nitrous oxide* gas or "laughing gas" and water, $NH_4NO_3 = N_2O + 2H_2O$.

Nitrous oxide is thus prepared for use as an anæsthetic. When required for inhalation, it is washed from any trace of acid or nitric oxide by being passed through solution of potash and solution of ferrous sulphate, the former absorbing acid vapours, the latter nitric oxide. It is slightly soluble in warm water, more so in cold. It supports combustion almost as well as oxygen. By pressure it may be liquefied to a colourless fluid, and by simultaneous cooling solidified.

Citrate, Phosphate, and Benzoate of Ammonium.

(The old Citrate, Phosphate, and Benzoate of Ammonia.)

Fourth Synthetical Reaction.—To solution of citric acid ($H_3C_6H_5O_7$) add solution of ammonia (NH_4HO) until the well-stirred liquid smells faintly of ammonia. Solutions having the specific gravities, respectively, of 1·062 and (four times the strength) 1·209, form the official Solutions of Citrate of Ammonium, $(NH_4)_3C_6H_5O_7$ (*Liquor Ammonii Citratis*, B.P., and *Liquor Ammonii Citratis Fortior*, B.P.).

Phosphate of Ammonium, $(NH_4)_2HPO_4$, (*Ammonii Phosphas*, B.P.), and *Benzoate of Ammonium* ($NH_4C_7H_5O_2$) (*Ammonii Benzoas*, B.P.), are also made by adding solution of ammonia to phosphoric acid (H_3PO_4) and benzoic acid ($HC_7H_5O_2$) respectively, evaporating (keeping the ammonia in slight excess by adding more of its solution), and setting aside for crystals to form.

$$\underset{\text{Citric acid.}}{H_3C_6H_5O_7} + \underset{\text{Ammonia.}}{3NH_4HO} = \underset{\text{Citrate of ammonium.}}{(NH_4)_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} + \underset{\text{Ammonia.}}{2NH_4HO} = \underset{\text{Phosphate of ammonium.}}{(NH_4)_2HPO_4} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Ammonia.}}{NH_4HO} = \underset{\text{Benzoate of ammonium.}}{NH_4C_7H_5O_2} + \underset{\text{Water.}}{H_2O}$$

Phosphate of ammonium occurs in transparent colourless prisms, soluble in water, insoluble in spirit; benzoate in crystalline plates, soluble in water and in spirit.

Bromide of Ammonium (B.P.) will be noticed in connection with Hydrobromic Acid and other Bromides.

Oxalate of Ammonium.

Fifth Synthetical Reaction.—To a nearly boiling solution of 1 part of oxalic acid in about 8 of water add carbonate of ammonium until the liquid is neutral to *test-paper* (*see* following paragraphs), filter while hot, and set aside for crystals to form. The product is Oxalate of Ammonium, B.P., $(NH_4)_2C_2O_4, H_2O$, the old Oxalate of Ammonia. The mother-liquor is useful as a reagent in analysis; 1 of the pure salt in 40 of water forms "Solution of Oxalate of Ammonium," B.P.

$$\underset{\text{Oxalic acid.}}{3H_2C_2O_4} + \underset{\text{“Carbonate of ammonium.”}}{2N_3H_{11}C_2O_5} = \underset{\text{Oxalate of ammonium.}}{3(NH_4)_2C_2O_4} + \underset{\text{Carbonic acid gas.}}{4CO_2} + \underset{\text{Water.}}{2H_2O}$$

Neutralization.—Thus far the methods by which the student has avoided excess of either acid matter on the one hand, or alkaline on the other, have been the rough aid of taste, cessation of effervescence, presence or absence of odour, etc. More delicate aid is afforded by *test-papers.*

Test-papers.—Litmus (B.P.) is a blue vegetable pigment, prepared from various species of *Roccella* lichen, exceedingly sensitive to the action of acids, which turn it red. When thus reddened, alkalies (potash, soda, and ammonia) and other soluble hydrates readily turn it blue. The student should here test for himself the delicacy of this action by experiments with paper soaked in solution of litmus and dipped into very dilute solutions of acids, acid salts ($KHC_4H_4O_6$, *e.g.*), alkalies, and such neutral salts as nitrate of potassium, sulphate of sodium, or chloride of ammonium.

Solution of Litmus (B.P.).—This is prepared from purified litmus. Gently boil litmus with three times its bulk of spirit of wine for an hour. Pour away the fluid and repeat the operation twice. Digest the residual litmus in distilled water and filter.

Blue litmus-paper (B.P.) is "unsized white paper steeped in solution of litmus and dried by exposure to the air." *Red litmus-paper* (B.P.) is "unsized white paper steeped in solution of litmus which has been previously reddened by the addition of a very minute quantity of acid, and dried by exposure to the air."

Turmeric paper (B.P.) similarly prepared from Tincture of Turmeric (B.P.) (1 of turmeric root or rhizome to 6 of rectified spirit, macerated for seven days), is occasionally useful as a test for alkalies, which turn its yellow to brown; acids do not affect it.

Other "indicators" of alkalinity or acidity are used.

Sulphydrate of Ammonium.

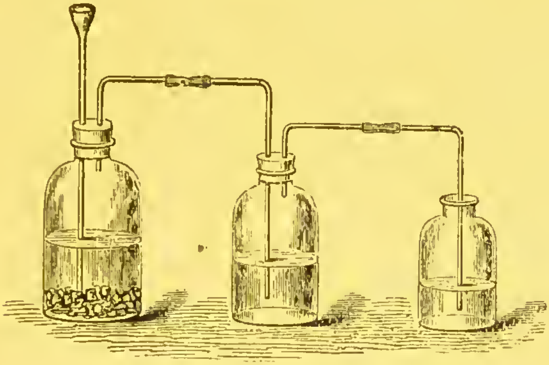
Sixth Synthetical Reaction.—Pass sulphuretted hydrogen gas (H_2S) through a small quantity of solution of ammonia in a test-tube, until a portion of the liquid no longer causes a white precipitate in solution of sulphate of magnesium; the product is Solution of Sulphydrate of Ammonium (NH_4HS), formerly erroneously termed Sulphide of Ammonium, a valuable chemical reagent, as will presently be apparent:—
$NH_4HO + H_2S = NH_4HS + H_2O$.

"*Solution of Sulphydrate of Ammonium*," of official strength, is made by passing the gas, prepared as described on the next page, into 3 fluid ounces of solution of ammonia (*Liquor Ammoniæ*) so long as the gas continues to be absorbed, then adding 2 more ounces of solution of ammonia, and preserving the solution in a well-stoppered bottle.

Sulphuretted hydrogen is a compound of noxious odour; hence the above operation, and many others, described farther on, in which this gas is indispensable, can only be performed in the open air, or in a *fume-cupboard*—a chamber so contrived that deleterious gases and vapours shall escape into a chimney in connection with the external air. In the above experiment, the small quantity of gas required can be made in a test-tube, after the manner of hydrogen itself. To some fragments of sulphide of iron (FeS) add water and then sulphuric acid; the gas is at once evolved, and may be conducted by a tube into the solution of ammonia. Sulphate of iron remains dissolved:—$FeS + H_2SO_4 = H_2S + FeSO_4$.

Sulphuretted-hydrogen Apparatus.—As no heat is necessary in making sulphuretted hydrogen (B.P.), the test-tube of the foregoing operation may be advantageously replaced by a bottle, especially when larger quantities of the gas are required. In analytical operations, the gas should be purified by passing it through water contained in a second bottle.

Fig. 18.



SULPHURETTED-HYDROGEN APPARATUS.

The most convenient arrangement for experimental use is prepared as follows:—Two common wide-mouth bottles are selected, the one having a capacity of about half a pint, the other a quarter pint; the former may be called the *generating-bottle*, the latter the *wash-bottle.* Fit two corks to the bottles. Through each cork bore two holes, with a round file or other instrument, of such a size that glass tubing of about the diameter of a quill pen shall fit them tightly. Through one of the holes in the cork of the generating-bottle pass a funnel-tube, so that its extremity may nearly reach the bottom of the bottle. To the other hole adapt a piece of tubing, 6 inches long, and bent in the middle to a right angle. A similar "elbow-tube" is fitted to one of the holes in the cork of the wash-bottle, and another elbow-tube, one arm of which is long enough to reach to near the bottom of the wash-bottle, fitted to the other hole. Removing the corks, two or three ounces of water are now poured into each bottle, an ounce or two of sulphide of iron put into the generating-bottle, and the corks replaced. The elbow-tube of the generating-bottle is now attached by a short piece of india-rubber tubing to the long-armed elbow-tube of the wash-bottle, so that gas coming from the generator may pass through the water in the wash-bottle. The delivery-tube of the wash-bottle is then lengthened by attaching to it, by india-rubber tubing, another piece of glass tubing, several inches in length. The apparatus is now ready for use. Strong sulphuric acid is poured down the funnel-tube in small quantities at a time, until brisk effervescence is established, and more added from time to time as the evolution of gas becomes slow. The gas passes through the tubes into the wash-bottle, where, as it bubbles up through the water, any trace of sulphuric acid, or other matter mechanically carried over, is arrested, and thence the gas flows out at the delivery-tube into any vessel or liquid that may be placed there to receive it. The generator must be occasionally dismounted, and the sulphate of iron washed out.

Luting (*lutum*, mud).—If the corks of the above apparatus are sound, and the tube-holes well made, no escape of gas will occur. If rough corks have been employed, or the holes are not cylindrical, linseed-meal lute may be rubbed over the defective parts. The lute is prepared by mixing linseed-meal with water to the consistence of dough. A neat appearance may be given to the lute by gently rubbing a well-wetted finger over its surface.

(c) *Reactions having Analytical Interest* (*Tests*).

First Analytical Reaction.—To a solution of a salt of ammonium (chloride, for example) in a test-tube, add solution of soda (or potash, or slaked lime), and well shake or warm; a characteristic odour (ammonia, NH_3) results:—
$NH_4Cl + NaHO = NH_3 + H_2O + NaCl$.

Though ammonium itself cannot be had in the free state, its compounds are stable. Ammonia is easily expelled from those compounds by action of the stronger alkalies, caustic potash, soda, or lime. As a matter of exercise, the student should here draw out equations in which acetate ($NH_4C_2H_3O_2$), sulphate, ($(NH_4)_2SO_4$), nitrate (NH_4NO_3), or any other ammoniacal salt, not already having the odour of ammonia, is supposed to be under examination; also equations representing the use of the other hydrates (KHO or Ca2HO).

The *odour* of ammonia is the best means of recognising its presence; but the following tests are occasionally useful. Into the upper part of the test-tube insert a glass rod moistened with strong hydrochloric acid (that is, with the solution of hydrochloric acid gas, conventionally termed hydrochloric acid, the *Acidum Hydrochloricum* of the Pharmacopœia); white fumes of chloride of ammonium will be produced :—$NH_3 + HCl = NH_4Cl$. Hold a piece of moist red litmus-paper in a tube in which is ammonia gas; the red colour will be changed to blue.

Second Analytical Reaction.—To a few drops of a solution of an ammonium salt add a drop or two of hydrochloric acid and a like small quantity of solution of perchloride of platinum ($PtCl_4$); a yellow crystalline precipitate (the double chloride of platinum and ammonium, $PtCl_4,2NH_4Cl$) will be produced similar in appearance to the corresponding salt of potassium, the remarks concerning which (p. 83) are equally applicable to the precipitate under notice.

Third Analytical Reaction.—To a moderately strong solution of an ammonium salt add a strong solution of tartaric acid, and shake or well stir the mixture; a white granular precipitate (acid tartrate of ammonium) will be formed.

For data from which to draw out an equation representing this action, see the remarks and formulæ under the analogous salt of potassium (p. 83).

Fourth Analytical Fact.—Evaporate a few drops of a solution of an ammonium salt to dryness, or place a fragment of a salt in the solid state on a piece of platinum foil, and heat in a flame; the salt is readily *volatilized.* As already noticed, the salts of potassium and sodium are *fixed* under these circumstances, a point of difference of which advantage will frequently be taken in analysis. A porcelain crucible may often be advantageously substituted for platinum foil in experiments on volatilization.

Salts of ammonium with the more complex acidulous radicals seldom volatilize unchanged when heated. The oxalate, when warmed, loses its water of crystallization, and at a higher temperature decomposes, yielding carbonic oxide, carbonic acid gas, ammonia gas, water (the three latter sometimes in combination), and several organic substances. The phosphate yields more or less phosphoric acid as a residue.

A wire triangle may be used in supporting crucibles (fig. 19). It is made by twisting together each pair of ends of three (5- or 6-inch) crossed pieces of wire (fig. 20). A piece of tobacco-pipe stem (about 2 inches) is sometimes placed in the centre of each wire before twisting, the transference of any metallic matter to the sides of the crucible being thus prevented (fig. 21).

Fig. 19.

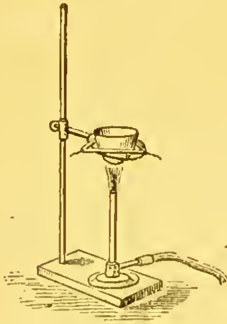


Fig. 20.

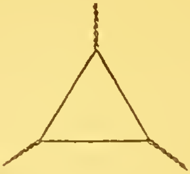
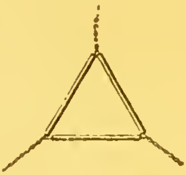


Fig. 21.



TRIANGULAR SUPPORTS FOR CRUCIBLES.

Practical Analysis.

With regard to those of the preceding experiments which are useful rather as means of detecting the presence of potassium, sodium, and ammonium, than as illustrating the preparation of salts, the so-called "tests," the student should proceed to apply them to certain solutions of any of the salts of potassium, sodium, and ammonium, with the view of ascertaining which metal is present; that is, proceed to *practical analysis.** A little thought will enable him to

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* Such solutions are prepared in educational laboratories by a tutor. They should, under other circumstances, be mixed by a friend, as it is not desirable for the student to know previously what is contained in the substance he is about to analyse.

The analysis of solutions containing only one salt serves to impress the apply these reactions in the most suitable order and to the best advantage for the contemplated purpose; but the following arrangements are perhaps as good as can be devised:—

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF **ONE** OF THE METALS, POTASSIUM, SODIUM, AMMONIUM.

To a small portion of the solution to be examined, in a test-tube, add caustic soda, and warm the mixture; the odour of ammonia gas reveals the presence of an ammonium salt.

If ammonium be not present, apply the perchloride-of-platinum test to another portion of the liquid; a yellow precipitate proves the presence of potassium.

(It will be observed that potassium can only be detected in the absence of ammonium, salts of the latter radical giving similar precipitates.)

The flame-test is sufficient for the recognition of sodium.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF **ONE, TWO, OR ALL THREE** OF THE ALKALI METALS.

Commence by testing a small portion of the solution for an ammonium salt. If it be present, make a memorandum to that effect, and then proceed to get rid of the ammoniacal compound to make way for the detection of potassium; advantage is here taken of the volatility of ammonium salts

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memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles. Medical students seldom have time to go farther than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all of the members of a group. Hence in this Manual two tables of short directions for analysing are given under each group. Pharmaceutical students should follow the second.

and the fixity of those of potassium and sodium. Evaporate the original solution to dryness in a small basin, transfer the solid residue to a porcelain crucible, and heat the latter to low redness, or until dense white fumes (of ammoniacal salts) cease to escape (*see* fig. 19). This operation should be conducted in a fume-cupboard, to avoid contamination of the air of the laboratory. When the crucible is cold, dissolve out the solid residue with a small quantity of hot water, and test the solution for potassium by the perchloride-of-platinum test, and for sodium by the flame-test.

When the starting test has shown absence of ammonium, the original solution may, of course, at once be tested for potassium and sodium.

Flame-test.—The violet tint imparted to flame by potassium salts may be seen when masked by the intense yellow colour due to sodium if the flame be observed through a piece of dark-blue glass, a medium which absorbs the yellow rays of light.

Note on Nomenclature.—The operations of *evaporation* and heating to redness, or *ignition*, are frequently necessary in analysis, and are usually conducted in the above manner. If vegetable or animal matter be also present, carbon is set free, and ignition is accompanied by *carbonization*; the material is said to *char*. When all carbonaceous matter is burnt off, the crucible being slightly inclined and its cover removed to facilitate combustion, and mineral matter, or *ash*, alone remains, the operation of *incineration* has been effected.

Note on the Classification of the Elements.—The compounds of potassium, sodium, and ammonium have many analogies. Their carbonates, phosphates, and other common salts are soluble in water. The atoms of the three radicals are univalent—that is, each displaces or is displaced by one atom of hydrogen. In fact, these radicals constitute by their similarity in properties a distinct group or family. All the elements thus naturally fall into classes—a fact that should constantly be borne in mind, and evidence of which should always be sought. It would be impossible for the memory to retain the details of Chemistry without a system of classification and leading principles. Classification is also an important feature in the art as well as in the science of Chemistry; for without it practical analysis could not be undertaken. The classification adopted in this volume is founded on the quantivalence of the elements and on their analytical relations.

QUESTIONS AND EXERCISES.

Why are ammoniacal salts classed with those of potassium and sodium?—Mention the sources of the ammonium salts.—Describe the characters of Chloride of Ammonium.—Give the formula of Sulphate of Ammonium.—Adduce evidence of the existence of Ammonium.—How is Solution of Ammonia prepared? Give a diagram.—How is the official Solution of Acetate of Ammonium prepared?—What is the composition of commercial Carbonate of Ammonium?—Define *sublimation.*—What ammoniacal salts are contained in *Spiritus Ammoniæ Aromaticus*, B.P., and *Spiritus Ammoniæ Fœtidus*, B.P.?—Give diagrams or equations illustrating the formation of Citrate, Phosphate, and Benzoate of Ammonium.—Give the formula of Oxalate of Ammonium.—How is hydrate of ammonium converted into sulphydrate?—Describe the preparation of Sulphuretted Hydrogen Gas.—Enumerate and explain the tests for ammonium.—How is potassium detected in a solution in which ammonium has been found?—Give equations illustrating the action of hydrate of sodium on acetate of ammonium; hydrate of potassium on sulphate of ammonium; and hydrate of calcium on nitrate of ammonium.—What are the effects of acids and alkalies on litmus and turmeric?—Describe the analysis of an aqueous liquid containing salts of potassium, sodium, and ammonium.—What meanings are commonly assigned to the terms *evaporation*, *ignition*, *carbonization*, and *incineration?*—Write a short article descriptive of the analogies of potassium, sodium, and ammonium, and their compounds.

BARIUM, CALCIUM, MAGNESIUM.

These three elements have many analogies. Their atoms are bivalent.

BARIUM.

Symbol, Ba. Atomic weight, 137.

The analytical reactions of this metal are those which are of chief interest to the general student of pharmacy. The nitrate of barium, the old nitrate of baryta or nitrate of barytes ($Ba2NO_3$), and the chloride ($BaCl_2,2H_2O$), are the soluble salts in common use in analysis (Chloride of Barium, B.P., and "Solution of Chloride of Barium," 1 in 10 of water, B.P.); and these and others are made by dissolving the native carbonate ($BaCO_3$), the mineral *witherite*, in acids, or by heating the other common natural compound of barium, the sulphate, *heavy white* or *heavy spar* ($BaSO_4$), with coal, which yields sulphide of barium (BaS), ($BaSO_4 + C_4 = 4CO + BaS$) and dissolving the sulphide in appropriate acids. When the nitrate is strongly heated, it is decomposed, the oxide of barium or *baryta* (BaO) remaining. Baryta, on being moistened, assimilates the elements of water with great avidity, and yields hydrate of barium (Ba2HO). The latter is tolerably soluble, giving *baryta water*; and from this solution crystals of hydrate of barium are obtained on evaporation.

The operations above described may all be performed in test-tubes and small porcelain crucibles heated by the gas-flame. Quantities of 1 oz. to 1 lb. require a coke furnace.

Peroxide of barium (BaO_2) is formed on passing air over baryta heated to about 600° F. On raising the temperature, oxygen is evolved and baryta remains. This is Boussingault's old process; but the baryta loses its absorbing power after a time. If the air be freed from carbonic acid gas, and the peroxide be not exposed to a much higher temperature than 800° F. (by heating in a vacuum), the baryta can be used over and over again. This improvement is by Messrs. Brin, who sell the oxygen compressed within strong metal cylinders. By the action of dilute acid, peroxide of barium yields solution of *peroxide of hydrogen* (H_2O_2), the old *oxygenated water*. On neutralizing solution of peroxide of hydrogen with ammonia, and adding permanganate of potassium, oxygen gas is evolved, its volume indicating the oxygen "volume-strength" of the original solution.

Quantivalence.—The atom of barium is bivalent, Ba''.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—To the aqueous solution of any soluble salt of barium (nitrate or chloride, for example) add dilute sulphuric acid; a white precipitate is obtained. Set the test-tube aside for two or three minutes, and when some of the precipitate has fallen to the bottom, pour away the supernatant liquid, wash the precipitate by adding water, shaking, setting aside, and again decanting; and then add strong nitric acid, and boil; the precipitate is insoluble.

The production of a white precipitate by sulphuric acid, insoluble even in hot nitric acid, is highly characteristic of barium. The name of this precipitate is sulphate of barium; its formula is $BaSO_4$.

Antidotes.—In cases of poisoning by soluble barium salts, obvious antidotes would be solution of alum or of any sulphates, such as those of magnesium and sodium (Epsom salt, Glauber's salt).

Second Analytical Reaction.—To a barium solution add solution of the yellow chromate of potassium (K_2CrO_4); a pale-yellow precipitate (chromate of barium, $BaCrO_4$) falls. Add acetic acid to a portion; it is insoluble. Add hydrochloric or nitric acid to another portion; it is soluble.

"*Neutral Chromate.*"—The red chromate (or bichromate) of potassium (K_2CrO_4, CrO_3) must not be used in this reaction, or the barium will be only imperfectly precipitated: for the red salt gives rise to the formation of free acid, in which chromate of barium is to some extent soluble:—

$$K_2CrO_4, CrO_3 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl.$$

The yellow chromate is obtained on adding bicarbonate of potassium, 200 grains, in small quantities at a time, to a hot solution of the red chromate, about 295 grains, until effervescence ceases. The product, diluted to 10 fluid ounces, is "Solution of Yellow Chromate of Potassium," B.P.

$$K_2CrO_4, CrO_3 + 2KHCO_3 = 2K_2CrO_4 + 2CO_2 + H_2O.$$

For analytical purposes solution of a *neutral chromate* is still more readily prepared by simply adding solution of ammonia to solution of red chromate of potassium, until the liquid turns yellow, and, after stirring, smells of ammonia.

$$K_2CrO_4, CrO_3 + 2NH_4HO = 2KNH_4CrO_4 + H_2O.$$

Other Analytical Reactions.—To a barium solution add a soluble carbonate (carbonate of ammonium—$(NH_4)_2CO_3$—will generally be rather more useful that the others); a white precipitate (carbonate of barium, $BaCO_3$) results. To more of the solution add an alkaline phosphate or arseniate (phosphate of sodium—Na_2HPO_4—is the most common of these chemically analogous salts, but phosphate of ammonium—$(NH_4)_2HPO_4$—or arseniate—$(NH_4)_2HAsO_4$—will subsequently have the preference); white phosphate of barium ($BaHPO_4$), insoluble in pure water, but slightly soluble in aqueous solutions of some salts, or arseniate of barium ($BaHAsO_4$), both soluble even in acetic and other weak acids, will be precipitated. To another portion add oxalate of ammonium $(NH_4)_2C_2O_4$; white oxalate of barium (BaC_2O_4) is precipitated, soluble in the diluted mineral acids, and sparingly so in acetic acid. Barium salts, moistened with hydrochloric acid, impart a greenish colour to flame.

Mem.—Good practice will be found in writing out equations descriptive of each of the foregoing reactions.

QUESTIONS AND EXERCISES.

What is the quantivalence of barium?—Write down the formulæ of oxide, hydrate, chloride, nitrate, and sulphate of barium ; and state how they are prepared.—Describe the preparation of peroxide of hydrogen.—Which of the tests for barium are most characteristic? give equations of the reactions.—Name the antidote in cases of poisoning by soluble barium salts, and explain its action.

CALCIUM.

Symbol, Ca. Atomic weight, 40.

Calcium compounds form a large proportion of the crust of our earth. Carbonate of calcium is met with as chalk, marble, limestone, calc-spar, etc.; the sulphate as gypsum and plaster of Paris (*Calcii Sulphas*, B.P., "native sulphate of calcium—$CaSO_4$, $2H_2O$—rendered nearly anhydrous by heat") and alabaster; the silicate in many minerals; the fluoride of calcium as fluor-spar. The phosphate is also a common mineral. The element itself is only isolated with great difficulty. The atom of calcium is bivalent, Ca″.

Reactions having Synthetical Interest.

Chloride of Calcium.

First Synthetical Reaction.—To some hydrochloric acid add carbonate of calcium (chalk, or the purer form, white marble, *Marmor Album*, B.P.) ($CaCO_3$) until effervescence ceases; filter; solution of chloride of calcium ($CaCl_2$), the most common soluble salt of calcium, is formed.

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	H_2O	+	CO_2
Carbonate of calcium.		Hydrochloric acid.		Chloride of calcium.		Water.		Carbonic acid gas.

This solution contains carbonic acid, and will give a precipitate of carbonate of calcium on the addition of lime-water. It may be obtained quite neutral by well boiling before filtering off the excess of marble. It is a serviceable test-liquid in analytical operations.

Solution of chloride of calcium evaporated to a syrupy consistence yields crystals ($CaCl_2$, $6H_2O$). These are extremely deliquescent. The solution, evaporated to dryness, and the white residue heated to about 200° C., gives solid chloride of calcium ($CaCl_2$, $2H_2O$) in a porous form. The resulting agglutinated lumps (*Calcii Chloridum*, B.P.) are used for drying gases and for freeing certain liquids from water. The salt is also soluble in alcohol. One part of this dried chloride with five of water forms the "Solution of Chloride of Calcium" (*Liquor Calcii Chloridi*, B.P.).

Mem.—The practical student has already met with solution of chloride of calcium as a by-product or secondary product in the preparation of carbonic acid gas.

Marble often contains ferrous carbonate ($FeCO_3$), which in the above process becomes converted into ferrous chloride, rendering the chloride of calcium impure :—

$FeCO_3$	+	$2HCl$	=	$FeCl_2$	+	H_2O	+	CO_2
Ferrous carbonate.		Hydrochloric acid.		Ferrous chloride.		Water.		Carbonic acid gas.

If absolutely pure chloride of calcium be required, a few drops of the solution should be poured into a test-tube or test-glass, diluted with water, and examined for iron (by adding sulphydrate of ammonium, which gives a black precipitate with salts of iron), and, if the latter is present, hypochlorite of calcium (in the form of chlorinated lime) and slaked lime be added to the remaining bulk of the liquid, and the whole boiled for a few minutes. Iron (as ferric hydrate) is thus precipitated; on filtering, a pure solution of chloride of calcium is obtained:—

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{4FeCl_2} + \underset{\substack{\text{Hypochlorite}\\\text{of calcium.}}}{Ca2ClO} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{4CaH_2O_2} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Ferric}\\\text{hydrate.}}}{2(Fe_26HO)} + \underset{\substack{\text{Chloride}\\\text{of calcium.}}}{5CaCl_2}$$

This is the official process, and may be imitated on the small scale after adding a minute piece of iron to a fragment of the marble before dissolving in acid.

The names, formulæ, and reactions of the compounds of iron will be considered later.

Oxide of Calcium. Quick Lime.

Second Synthetical Reaction.—Place a small piece of chalk in a strong grate-fire or furnace, and heat until a trial fragment, chipped off and cooled, no longer effervesces on the addition of acid; caustic lime, CaO (*Calx*, B.P.), remains.

$$\underset{\substack{\text{Carbonate of}\\\text{calcium (chalk).}}}{CaCO_3} = \underset{\substack{\text{Oxide of}\\\text{calcium (lime).}}}{CaO} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Note.—Etymologically considered, this action is analytical (ἀναλύω, *analuō*, I resolve), and not synthetical (σύνθεσις, *sunthĕsis*, a putting together); but conventionally it is synthetical and not analytical; for in this, the usual sense, synthesis is the application of chemical action with the view of producing something; analysis, the application of chemical action with the view of finding out the composition of a substance. In the etymological view of the matter, there is scarcely an operation performed, either by the analyst or by the manufacturer, but includes both analysis and synthesis—that is, includes interchange or *metathesis*.

Lime-kilns.—On a large scale the above operation is carried on in what are termed *lime-kilns* (*Kiln*, Saxon *cyln*, from *cylene*, a furnace).

Hydrate of Calcium. Slaked Lime.

Slaked Lime.—When cold, add to the lime about half its weight of water, and notice the evolution of steam and other evidence of strong action; the product is *slaked* lime, hydrate of calcium (Ca2HO) (*Calcii Hydras*, B.P.), the old Hydrate of Lime, with whatever slight natural impurities the lime may contain. The slaking of hard or "stony" lime may be accelerated by using hot water.

$$\underset{\text{Lime.}}{CaO} \quad + \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Hydrate of calcium.}}{Ca2HO}$$

Lime-water.—Place the hydrate of calcium (washed with a little water to remove traces of soluble salts) in about a hundred times its weight of water; in a short time a saturated solution, known as *lime-water* (*Liquor Calcis*, B.P.), results. It contains about 13 grains of hydrate of calcium (Ca2HO), equivalent to about 10 grains of lime (CaO), in one pint at 60° F. At higher temperatures less is dissolved.

Strong Solution of Lime.—Slaked lime is more soluble in aqueous solution of glycerine and much more soluble in aqueous solution of sugar than in pure water. The *Liquor Calcis Saccharatus*, B.P., is such a solution, containing 2 ounces of sugar, and 188 grains of hydrate of calcium (Ca2HO), equivalent to 142 grains of lime (CaO), in 1 pint. It is a more efficient precipitant of hydrates, carbonates, and phosphates than lime-water. The official process is as follows:—Mix 1 ounce of lime and 2 of sugar by trituration in a mortar. Transfer the mixture to a bottle containing 1 pint of water, and, having closed this with a cork, shake it occasionally for a few hours. Finally separate the clear solution with a siphon, avoiding unnecessary exposure to air, and keep it in a well-stoppered bottle.

Solutions of hydrate of calcium absorb carbonic acid gas on exposure to air, a semi-crystalline precipitate of carbonate being deposited. When the saccharated solution is heated, there is precipitated a compound consisting of three molecules of lime with one of sugar. When it is freely exposed to air, oxygen is absorbed, and the solution becomes coloured.

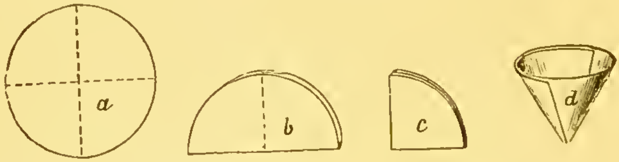
Carbonate of Calcium.

Third Synthetical Reaction.—To a solution of chloride of calcium add excess of carbonate of sodium, or about 5 parts of dry chloride to 13 of carbonate; a white precipitate of carbonate of calcium (*Calcii Carbonas Præcipitata*, B.P., the old Precipitated Carbonate of Lime) ($CaCO_3$) results. If the solutions of the salts be made hot before admixture, and the whole be set aside for a short time, the particles aggregate to a greater extent than when cold water is used, and the product is finely granular or slightly crystalline. The official variety is thus prepared.

$$\underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Carbonate of calcium.}}{CaCO_3} + \underset{\text{Chloride of sodium.}}{2NaCl}$$

Collect and purify this *Precipitated Chalk* by pouring the mixture into a paper cone supported by a funnel, and, when the liquid has passed through the filter, pour water over the precipitate three or four times, until the whole of the chloride of sodium is washed away. This operation is termed *washing a precipitate*. When dried by aid of a *water-bath* (p. 122) or other means, the precipitate is fit for use.

Fig 22.



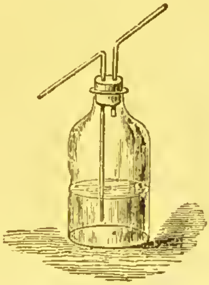
CONSTRUCTION OF PAPER FILTERS.

Filtering paper, or *bibulous paper* (from *bibo*, I drink), is simply good unsized paper made from the best white rags—white blotting-paper, in fact, of unusually good quality. Students' or analysts' filters, on which to collect precipitates, are *circular* pieces (*a*, fig. 22) of this paper, from three to six inches in diameter, twice folded (*b*, *c*), and then opened out so as to form a hollow cone (*d*). Square pieces of filter paper are rounded by scissors *after* twice folding. The cone is supported by a glass or earthenware funnel.

Filters should *always* be cut round, so as to form a cone. If the square piece of paper is folded and used without being so cut or trimmed, an ugly angular filter results, from which it is difficult to wash all "mother-liquor" (the solution of chloride of sodium is the "mother-liquor" in the previous reaction). Moreover, if a spirituous or other volatile fluid is being passed through such an angular filter, much of the liquid will also be wasted by evaporation from the unnecessarily large surface exposed.

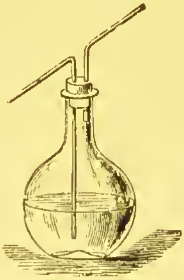
Paper filters of large size are apt to break at the point of the cone. This may be prevented, and the rate of filtration be much accelerated, by supporting the paper cone in a cone of muslin.

Fig. 23.



WASHING-BOTTLE.

Fig. 24.



WASHING-FLASK.

Washing-bottle.—Precipitates are best washed by a fine jet of water directed on to the different parts of the filter. A common, narrow-necked bottle, of about half-pint capacity (fig. 23), is fitted with a cork; two holes are bored through the cork, the one for a glass tube reaching to the bottom of the bottle within, and externally bent to a slightly acute angle, the other for a tube bent to a slightly obtuse angle, the inner arm terminating just within the bottle. The outer arms may be about three inches in length. The extremity of the outer arm continuous with the longer tube should be previously drawn out to a fine capillary opening by holding the original tube (before bending) in a flame, and, when soft, slowly pulling the halves away from each other until the heated portion is reduced to the thinness of a knitting-needle. The tube is now cut at the thin part by a file, and the sharp edges rounded off by placing in a flame for a second or two. The outer extremity of the shorter tube should also be made smooth in the flame. The apparatus being put together, and the bottle nearly filled with water, air blown through the short tube by the lungs forces water out in a fine stream at the capillary orifice.

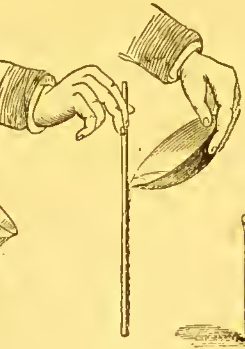
For a hot-water washing-flask (fig. 24) the tubes and cork are fitted to a flask which may be heated. A strip of thin leather tied round the neck will protect the fingers.

Decantation.—Precipitates may also be washed by allowing them to settle, pouring off the supernatant liquid (fig. 25) agitating with water, again allowing to settle, and so on. This is washing by *decantation* (*de*, from; *canthus*, an edge). If a stream of liquid flowing from a basin or other vessel exhibits any tendency to run down the outer side of the vessel, it should be guided by a glass rod placed against the point whence the stream emerges (fig. 26).

Fig. 25.

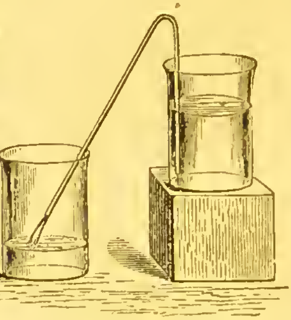
DECANTATION.

Fig. 26.



DECANTATION.

Fig. 27.



SIPHON IN ACTION.

If the vessel be too large to handle with convenience, the wash-water may be drawn off by a *siphon*, as shown in miniature in fig. 27. A siphon is a tube of glass, metal, gutta-percha, or india-rubber, bent into the form of a V or U, filled with water and inverted. One end is immersed in the wash-water, and the other allowed to hang over the side of the vessel. So long as the outer orifice of the instrument is below the level of any liquid in the vessel, so long will that liquid flow from within outwards.*

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* *The nature of the action of a siphon* is simple. The column of water in the outer limb is longer, and therefore heavier, than the column of similar area in the inner limb. (The length of the inner limb must be reckoned from the surface of the liquid, the portion below the surface playing no part in the operation.) Being heavier, it naturally falls by gravitation, the liquid in the shorter limb instantly following because pressed upwards by the air. The air, be it observed, exerts a similar amount of pressure on the liquid in the outer limb; in short, atmospheric pressure causes the retention of liquid in the instrument, while gravitation determines the direction of the flow.

Prepared carbonate of calcium (*Creta Præparata*, B.P.) is merely washed chalk (*Creta*, B.P.) or *whiting*, only that in pharmacy fashion demands that the chalk be in little conical lumps, about the size of thimbles, instead of in the larger rolls characteristic of "whiting." Wet whiting pushed, portion by portion, through a funnel, and each separately dried, gives the conventional *Creta Præparata.* Its powder is amorphous.

If either the precipitated or the prepared carbonate of calcium contains alumina, magnesian salts, oxide of iron, or phosphates, its solution in acid, evaporated and re-dissolved in water, will yield a precipitate of hydrates or phosphates on the addition of saccharated solution of lime.

Phosphate of Calcium.

Fourth Synthetical Reaction.—Digest bone-ash (bones burnt in an open crucible with free access of air until all animal and carbonaceous matter has been removed—impure phosphate of calcium—*Os Ustum*, B.P.) with twice its weight of hydrochloric acid (diluted with four times its bulk of water) in a test-tube or larger vessel; the phosphate is dissolved.

$$\underset{\text{Phosphate of calcium (impure).}}{Ca_3 2PO_4} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Acid phosphate of calcium.}}{CaH_4 2PO_4} + \underset{\text{Chloride of calcium.}}{2CaCl_2}$$

Dilute with water, boil, filter, and, when cold, add excess of solution of ammonia; the phosphate of calcium, now practically pure (*Calcii Phosphas*, B.P.), the old Phosphate of Lime, is reprecipitated as a light white amorphous powder. After well washing, the precipitate should be dried over a *water-bath* (*see* next page), or at a temperature not exceeding 212° F., to prevent undue aggregation of the particles.

$$\underset{\text{Acid phosphate of calcium.}}{CaH_4 2PO_4} + \underset{\text{Chloride of calcium.}}{2CaCl_2} + \underset{\text{Ammonia.}}{4NH_4HO} = \underset{\text{Phosphate of calcium (pure).}}{Ca_3 2PO_4} + \underset{\text{Chloride of ammonium.}}{4NH_4Cl} + \underset{\text{Water.}}{4H_2O}$$

Bone-ash or bone-earth contains small quantities of carbonate and sulphide of calcium. These are decomposed in the above process by the acid, chloride of calcium being formed; on boiling the mixture, carbonic acid gas and sulphuretted hydrogen gas are evolved. Any carbonaceous or siliceous matter, etc., is removed by filtration. In bones the phosphate of calcium is always accompanied by a small quantity of an allied substance, phosphate of magnesium: a trace of fluoride of calcium (CaF_2) is also present.

A *Water-bath* for the evaporation of liquids or for drying moist solids at temperatures below 212° F., is an iron, tin, or earthenware pan, the mouth of which can be narrowed by iron or tin diaphragms of various sizes, and having orifices adapted to the diameters of basins or plates. (*See* fig. 16, p. 73.) In the British Pharmacopœia, "when a *water-bath* is directed to be used, it is to be understood that this term refers to an apparatus by means of which water or its vapour, at a temperature not exceeding 212°, is applied to the outer surface of a vessel containing the substance to be heated, which substance may thus be subjected to a heat near to, but necessarily below, that of 212°. In the *steam-bath*, the vapour of water at a temperature above 212°, but not exceeding 230°, is similarly applied." Evaporation *in vacuo* is performed by simply placing the vessel of liquid over or by the side of a small reservoir of strong sulphuric acid, or other absorbent of moisture, on the plate of an air-pump, covering with a capacious glass hood or "receiver," and exhausting.

Bone-black, or *Animal Charcoal* (*Carbo Animalis*, B.P.), is the residue obtained on subjecting dried bones to a red heat without access of air. It is a mixture of about 9 parts of mineral matter with 1 of carbonaceous matter. The operation may be imitated by heating a few fragments of bone in a covered porcelain crucible in a fume chamber until smoke and vapour cease to be evolved. Purified Animal Charcoal (*Carbo Animalis Purificatus*, B.P.) may be obtained as follows:—Boil powdered animal charcoal with a mixture of twice its weight of hydrochloric acid, and twice its weight of water; filter; again boil the drained residue with half the amount of such diluted acid as was previously employed; again filter; wash the residual charcoal with distilled water until the washings give little or no turbidity with solution of nitrate of silver; dry the product in a warm place. It should not yield more than 10 per cent. of moisture when dried at a high temperature, nor more than 15 per cent. of ash when thoroughly incinerated. Thirty grains well shaken with 15 ounces of distilled water containing 0·005 per cent. of ordinary commercial caramel should remove at least four-fifths of the colour from the fluid. (Hodgkin.)

Wood Charcoal (*Carbo Ligni*, B.P.) is wood similarly ignited without access of air. On incineration it yields about two per cent. of ash.

Decolorizing power of Animal Charcoal.—Animal charcoal, in small fragments, is the material employed in decolorizing solutions of common brown sugar, with the view of producing white lump sugar. Its power, and the nearly equal power of an equivalent quantity of the purified variety, may be demonstrated on solution of litmus or logwood.

Phosphate of Sodium.—Phosphate of calcium is converted into phosphate of sodium (*Sodii Phosphas*, B.P., the old Phosphate of Soda) (Na_2HPO_4, $12H_2O$) as follows:—Mix, in a mortar, 3 ounces of ground bone-earth with 1 fluid ounce of sulphuric acid; set aside for twenty-four hours to promote reaction; mix in about 3 ounces of water, and put in a warm place for two days, a little water being added to make up for that lost by evaporation; stir in another 3 ounces of water, warm the whole for a short time, filter, and wash the residual sulphate of calcium on the filter to remove adhering acid phosphate of calcium; concentrate the *filtrate* (the liquid portion), which is a solution of acid phosphate of calcium, to about 3 ounces, filter again if necessary, add solution of (about 4½ ounces of crystals of) carbonate of sodium to the hot filtrate until a precipitate (a phosphate of calcium, $CaHPO_4$) ceases to form, and the fluid is faintly alkaline; filter, evaporate, and set aside to crystallize.

Phosphate of sodium occurs "in transparent, colourless, rhombic prisms, terminated by four converging planes; efflorescent, tasting like common salt." One part in ten of water constitutes "Solution of Phosphate of Sodium," B.P.

The following equations show the two decompositions which occur during the operations:—

$$\underset{\text{Phosphate of calcium.}}{Ca_32PO_4} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Acid phosphate of calcium.}}{CaH_42PO_4} + \underset{\text{Sulphate of calcium.}}{2CaSO_4}$$

$$\underset{\text{Acid phosphate of calcium.}}{CaH_42PO_4} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Phosphate of sodium.}}{Na_2HPO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2} + \underset{\text{Monocalcic phosphate.}}{CaHPO_4}$$

Ordinary phosphate of sodium (Na_2HPO_4, $12H_2O$) effloresces rapidly in the air until nearly half its water has escaped, when it has a permanent composition represented by the formula $Na_2HPO_4,7H_2O$. Phosphate of sodium has an alkaline reaction. Neutralization by acid results in the removal of half its sodium and formation of the salt NaH_2PO_4, H_2O.

Hypochlorite of Calcium.

Fifth Synthetical Reaction.—Pass chlorine, generated as already described, into damped slaked lime contained in a piece of wide tubing, open at the opposite end to that in which the delivery-tube is fixed. (A test-tube, the bottom of which has been accidentally broken, is very convenient for such operations.) The product is ordinary *bleaching-powder*, a compound of hypochlorite and chloride of calcium, commonly called *chloride of lime*, the *Calx Chlorinata* of the British Pharmacopœia.

$$\underset{\text{Black oxide of manganese.}}{MnO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Chloride of manganese.}}{MnCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}$$

$$\underset{\text{Hydrate of calcium.}}{2CaH_2O_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Water.}}{2H_2O} + \overset{\text{Chlorinated lime.}}{\underset{\text{Hypochlorite of calcium.}}{CaCl_2O_2}, \underset{\text{Chloride of calcium.}}{CaCl_2}}$$

Chlorinated lime exposed to air and moisture, as in disinfecting the atmosphere of sick-rooms, slowly yields hypochlorous acid (HClO). Free hypochlorous acid soon breaks up into water, chloric acid ($HClO_3$), and free chlorine. Chloric acid is also unstable, decomposing into oxygen, chlorine, water, and perchloric acid ($HClO_4$). The small quantity of hypochlorous acid diffused through an apartment when bleaching-powder is exposed thus yields fourteen-fifteenths of its chlorine in the form of chlorine gas—one of the most efficient of known disinfectants.

Constitution of bleaching-powder.—Treated with alcohol, bleaching-powder does not yield its chloride of calcium to the solvent; hence the powder is not a mere mixture of chloride and hypochlorite of calcium: water, also, does not dissolve out first one salt and then the other, but both together, in the molecular proportions of the above formula. On the other hand, when the aqueous solution is cooled, or evaporated *in vacuo*, crystals are obtained which Kingzett has shown to be nearly pure hypochlorite of calcium, the solution containing chloride of calcium. While the former fact indicates that the powder is a compound, and not a mere mixture, the latter indicates that it is a feeble compound—an adhesion of molecules of hypochlorite and chloride, as shown in the equation, rather than any more intimate or closer combinations of atoms. If it be regarded as a single rather than a double salt, then the following formula may be employed, $CaOCl_2$, or $Ca\left\{\begin{array}{l}Cl\\ClO.\end{array}\right.$

Bleaching-liquor.—Digest chlorinated lime in water, in which the bleaching compound is soluble, filter from undissolved lime, etc., and test the bleaching powers of the clear liquid by adding a few drops to a decoction of logwood slightly acidulated. One pound of this bleaching-powder, shaken several times during three hours with 1 gallon of water, forms the official Solution of Chlorinated Lime (*Liquor Calcis Chlorinatæ*, B.P.).

Sixth Synthetical Reaction.—Mix a little powdered wood charcoal with three or four times its weight of plaster of Paris, and heat to redness in a crucible. Some of the sulphate is reduced to sulphide of calcium (CaS) with production of carbonic acid and carbonic oxide gases. If the product contains not less than fifty per cent. of sulphide of calcium and no carbon, it is the official Sulphurated Lime (*Calx Sulphurata*, B.P.).

Official test of strength.—"If eight grains be added to a cold solution of fourteen grains of sulphate of copper in an ounce of water, a little hydrochloric acid be added, and the mixture be then well stirred and heated to a temperature approaching that of ebullition until all action has ceased, the filtered liquid should give no red colour with ferrocyanide of potassium."

The explanation of the mode of action of this test is as follows :—Sulphate of copper and sulphide of calcium, in the presence of the acid, react on each other, giving insoluble sulphide of copper and sulphate of calcium, thus:—

$$CuSO_4, 5H_2O + CaS = CuS + CaSO_4, 2H_2O + 3H_2O.$$

On adding up the atomic weights of the constituent elements of crystallized sulphate of copper, 249·5 will be found to be the molecular weight; while CaS will similarly represent 72 parts. As 249·5 are to 72, so are 14 to 4. But only half of the sulphurated lime is sulphide of calcium; therefore 8 grains of such sulphurated lime will react with 14 of sulphate of copper. If the 8 grains are below the stated strength, then they will not attack 14 grains of the copper salt, and, in that case, ferrocyanide of potassium will reveal copper in the filtered liquid.

Gummate of Calcium.

Gummate of Calcium is the only official calcium salt that remains to be noticed. This compound is, in short, *arabin*, the ordinary Gum-Acacia or Gum-Arabic (*Acaciæ Gummi*, B.P.), a substance too well known to need description. A solution of gum-arabic in water (*Mucilago Acaciæ*, B.P.) yields a white precipitate of oxalate of calcium on the addition of solution of oxalate of ammonium. Or a piece of gum burnt to an ash in a porcelain crucible yields a calcareous residue, which, dissolved in dilute acids, affords characteristic reactions with any of the following analytical reagents for calcium. In some specimens of gum-arabic a portion of the calcium is displaced by an equivalent quantity of potassium or magnesium. The gummic or arabic radical may be precipitated as opaque gelatinous gummate of lead by the addition of solution of oxyacetate of lead (*Liquor Plumbi Subacetatis*, B.P.) to an aqueous solution of gum. These statements should be experimentally verified.

Tragacanth (*Tragacantha*, B.P.) is a mixture of soluble arabinoid gum and a variety of calcium gum insoluble in water, termed *bassorin*. With water, a gelatinous mucilage is formed (*Mucilago Tragacanthæ*, B.P.).

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add sulphuric acid, *very* highly diluted, to a calcium solution contained in a test-tube or small test-glass; sulphate of calcium ($CaSO_4$, $2H_2O$) is formed, but is *not* precipitated, it being, unlike sulphate of barium, slightly soluble in water.

Solution of Sulphate of Calcium.—A quarter of an ounce of that (dried) form of sulphate of calcium known as plaster of Paris ($CaSO_4$) digested in one pint of water for a short time, with occasional shaking, and the mixture filtered, yields the official test-liquid termed "Solution of Sulphate of Calcium," B.P. About 400 parts of the solution contain 1 of sulphate of calcium.

Second Analytical Reaction.—Add yellow chromate of potassium (K_2CrO_4) or other neutral chromate (KNH_4CrO_4) to a calcium solution slightly acidified with acetic acid; chromate of calcium ($CaCrO_4$) may be formed, but is *not* precipitated. Barium is precipitated by the chromate.

These two negative reactions are most valuable in analysis, as every precipitant of calcium is also a precipitant of barium; but the above two reagents are precipitants of barium only. Hence, calcium, which when alone can be readily detected by the following reactions, cannot by any reaction be detected in the presence of barium. But by the sulphuric or chromic test, barium is easily removed, and then either of the following reagents will throw down the calcium.

Other Analytical Reactions.—Add carbonate of ammonium, phosphate of sodium, arseniate of ammonium, and oxalate of ammonium to calcium solutions, as described under the analytical reactions of barium, and write out descriptive equations. The precipitates correspond in appearance to those of barium; their constitution is also similar, hence their correct formulæ can easily be deduced. Of these precipitants, oxalate of ammonium is that most commonly used as a reagent for calcium salts, barium being absent. The oxalate of calcium is insoluble in acetic, but soluble in hydrochloric or nitric acids. Calcium compounds impart a reddish colour to flame.

QUESTIONS AND EXERCISES.

Enumerate some of the common natural compounds of calcium.—Explain, by an equation, the action of hydrochloric acid on marble. What official compound results?—Why is chloride of calcium used as a desiccator for gases?—How would you purify Chloride of Calcium which has been made from ferruginous marble? Give diagrams.—Write a few lines on the chemistry of the lime-kiln.—In what sense is the conversion of chalk into lime an analytical action?—What occurs when lime is "slaked"?—To what extent is lime soluble in water (*Liquor Calcis*, B.P.)? to what in Syrup (*Liquor Calcii Saccharatus*, B.P.)?—Describe the preparation of the official Precipitated Carbonate of Calcium (*Calcii Carbonas Præcipitata*, B.P.); in what does it differ from Prepared Chalk (*Creta Præparata*, B.P.)?—In what does filtering-paper differ from other kinds of paper?—Explain the construction of a "washing-bottle" for cleansing precipitates by water.—Define *decantation.*—Describe the construction and manner of employment of a siphon.—Explain the mode of action of a siphon.—State the difference between *Os Ustum* and *Calcii Phosphas.*—How is "bone-earth" purified for use in medicine?—Explain the action of hydrochloric acid on animal charcoal in the processes of purification.—What is the chemical difference between *Carbo Animalis*, B.P., and *Carbo Ligni*, B.P.?—Give equations showing the conversion of Phosphate of Calcium into Phosphate of Sodium.—Write a short article on the manufacture, composition, and uses of "bleaching-powder" (*Calx Chlorinata*, B.P.).—How may calcium be detected in Gum-Arabic?—State the chemical nature of Tragacanth.—To what extent is sulphate of calcium soluble in water?—Can calcium be detected in a solution containing barium?—Barium being absent, what reagents may be used for the detection of calcium? Which is the chief test?

MAGNESIUM.

Symbol, Mg. Atomic weight, 24.

Source.—Magnesium is abundant in nature as magnesian or mountain limestone, termed *dolomite* (after Dolomieu, a geologist), a double carbonate of magnesium and calcium in very common use as a building-stone (*e.g.* the Houses of Parliament and the School of Mines, in London), and *magnesite*, a tolerably pure carbonate of magnesium, though too "stony" for direct use in medicine, even if very finely powdered. Chloride of magnesium and sulphate of magnesium (Epsom salt) also occur in sea-water and the water of many springs. A monohydrous sulphate ($MgSO_4$, H_2O), termed *kiescrite*, occurs near Stassfurt, in Prussia. Metallic magnesium may be obtained from the chloride by the action of sodium. It burns readily in the air, emitting a dazzling light due to the white heat to which the resulting particles of magnesia (MgO) are exposed. The chloride employed as a source of the metal is obtained by dissolving the carbonate in hydrochloric acid, adding some chloride of ammonium, evaporating to dryness, heating the residue in a deep vessel (on the small scale, a large test-tube or flask) until the chloride of ammonium is all volatilized, and the chloride of magnesium remains as a clear fused liquid. The latter is poured on to a clean earthenware slab. The chloride of ammonium prevents reaction between chloride of magnesium and water in the last stages of the operation, and consequent formation of oxide (or oxychloride) of magnesium and hydrochloric acid gas.

Quantivalence.—The atom of magnesium is bivalent, Mg''.

Reactions having Synthetical Interest.

Sulphate of Magnesium.

First Synthetical Reaction.—To a few drops of sulphuric acid and a little water in a test-tube, made hot (or to larger quantities in larger vessels), add powdered native carbonate of magnesium, *magnesite*, $MgCO_3$, until effervescence ceases, subsequently boiling to aid in the expulsion of the carbonic acid gas. The filtered liquid is a solution of sulphate of magnesium ($MgSO_4$), crystals of which, *Epsom salt* ($MgSO_4$, $7H_2O$) (*Magnesii Sulphas*, B.P., the old Sulphate of Magnesia) may be obtained on evaporating most of the water, and setting the concentrated solution aside to cool. This is an ordinary manufacturing process. Instead of magnesite *dolomite*, the common magnesian limestone (carbonate of magnesium and of calcium—$CaCO_3$, $MgCO_3$), may be employed, any iron being removed by evaporating the solution (filtered from the sulphate of calcium produced) to dryness, gently igniting to decompose sulphate of iron, dissolving in water, filtering from oxide of iron, and crystallizing. (If neither mineral be at hand, the practical student may use a little of the ordinary manufactured carbonate of pharmacy; for the chemical action is almost identical, and it is the chemistry, and not, just now, the commercial economy of the matter, that he is studying. The manufacturer must, of course, commence with one of the above mineral carbonates furnished by Nature, from that make his sulphate, and from the latter, as will be seen directly, make the pure pulverulent carbonate of pharmacy.)

$$\underset{\text{"Magnesite."}}{MgCO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\\text{magnesium.}}}{MgSO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{CO_2}$$

Sulphate of magnesium readily crystallizes in large, colourless, transparent, rhombic prisms; but, from concentrated solutions, the crystals are deposited in short, thin needles, a form more convenient for manipulation, solution, and general use in medicine.

Iron may be detected in sulphate of magnesium by adding the common alkaline solution of chlorinated lime or chlorinated soda to some aqueous solution of the salt; brown hydrate of iron ($Fe_2 6HO$) is then precipitated. Sulphydrate of ammonium will also give a black precipitate if iron be present.

Effervescent Sulphate of Magnesium (*Magnesii Sulphas Effervescens*, B.P.) is sulphate of magnesium out of which nearly half its water of crystallization has been dried, and then mixed with citric and tartaric acids and sugar.

Carbonates of Magnesium.

Second Synthetical Reaction.—To solution of sulphate of magnesium, add solution of carbonate of sodium, and boil; the resulting precipitate is *light* carbonate of magnesium (*Magnesii Carbonas Levis*, B.P.), the old Light Carbonate of Magnesia, a white, partly amorphous, partly minutely crystalline mixture of carbonate and hydrate of magnesium ($3MgCO_3, Mg2HO, 4H_2O$). A denser, slightly granular precipitate of similar chemical composition (*Magnesii Carbonas Ponderosa*, B.P.), the old Heavy Carbonate of Magnesia, is obtained on mixing strong solutions of the above salts, evaporating to dryness, then removing the sulphate of sodium by digesting the residue in hot water, filtering, washing, and drying the precipitate.

$4MgSO_4$	$+\ 4Na_2CO_3$	$+\ H_2O$	$=\ 3MgCO_3, Mg2HO$	$+\ 4Na_2SO_4$	$+\ CO_2$
Sulphate of magnesium.	Carbonate of sodium.	Water.	Official Carbonate of magnesium.	Sulphate of sodium.	Carbonic acid gas.

The official proportions for the light carbonate are 10 of sulphate of magnesium and 12 of crystals of carbonate of sodium, each dissolved in 80 of cold water, the solutions mixed, boiled for 15 minutes, the precipitate collected on a filter, well washed, drained, and dried over a water-bath. The heavier carbonate is made with the same proportions of salts, each dissolved in 20 instead of 80 of water, the mixture evaporated quite to dryness, and the residue washed by decantation or filtration until all sulphate of sodium is removed (shown by a white precipitate—sulphate of barium—ceasing to form on the addition of solution of chloride or nitrate of barium to a little of the filtrate).

Another (*Pattinson's*) *Process.*—Considerable quantities of carbonate of magnesium are now prepared by treating dolomite (p. 129) with carbonic acid gas under pressure. Of the two carbonates, that of magnesium is dissolved first, and is precipitated from the clear liquid by the heat of a current of steam. (*See* next reaction.)

Third Synthetical Reaction.—Pass carbonic acid gas, generated as described on page 74, into a mixture of water and carbonate of magnesium contained in a test-tube.

After some time, separate any undissolved carbonate by filtration; the filtrate contains *normal* carbonate of magnesium ($MgCO_3$, $3H_2O$) dissolved in carbonic acid. When of a strength of about 10 grains of *official* carbonate in one ounce, such a solution constitutes "*Fluid Magnesia*" (*Liquor Magnesii Carbonatis*, B.P.). It is possible to obtain a strength of about 3 per cent. at about 55° F., which is reduced to 2½ per cent. at 70° and to about 2 per cent. at 80°.

Officially 1 pint is directed to be made from freshly prepared carbonate. The latter is obtained by adding a hot solution of 2 ounces of sulphate of magnesium in half-a-pint of water to one of 2½ ounces of crystals of carbonate of sodium in another half-pint of water, boiling the mixture for a short time (to complete decomposition), filtering, thoroughly washing the precipitate, placing the latter in 1 pint of distilled water, and transmitting carbonic acid gas through the liquid (say, at the rate of three or four bubbles per second) for an hour or two, then leaving the solution in contact with the gas under pressure of about three atmospheres for twenty-four hours, and, finally, filtering from undissolved carbonate; then, after passing in a little more gas, keeping in a well-corked bottle. Slight pressure is best produced by placing the carbonate and water in a bottle fitted with a cork and tubes as for a wash-bottle (p. 105), conveying the gas by the tube which reaches to the bottom, and allowing excess of gas to flow out by the upper tube, the external end of which is continued to the bottom of a common phial containing about an inch of mercury. The phial should be loosely plugged with cotton wool, to prevent loss of metal by spurting during the flow of the gas through it. (Each inch in depth of mercury through which the gas escapes corresponds to about half-a-pound pressuro on every square inch of surfaco within the apparatus.)

Heat a portion of the solution: true carbonate of magnesium containing combined water ($MgCO_3$, $3H_2O$) is precipitated. The water in this compound is probably in the state of water of crystallization, for a salt having the same composition is deposited in crystals by the spontaneous evaporation of the solution of carbonate of magnesium. The official "carbonate" ($3MgCO_3$, $Mg2HO$, $4H_2O$) is another of these very common *hydrous* compounds.

Exposed to cold, the solution of "fluid magnesia" sometimes affords large thick crystals ($MgCO_3, 5H_2O$), which, in contact with the air, lose water, become opaque, and then have the composition of those deposited by evaporation ($MgCO_3, 3H_2O$).

It is difficult to understand the *constitution* of the official carbonate. It is probably a single molecule, of the constitution of which we are at present ignorant.

Oxide of Magnesium. Magnesia.

Fourth Synthetical Reaction.—Heat light dry carbonate of magnesium in a porcelain crucible over a lamp (or in a larger earthen crucible in a furnace) till it ceases to effervesce on adding water and acid to a small portion; the residue is light magnesia (MgO) (*Magnesia Levis*, B.P.). The same operation on the heavy carbonate yields heavy magnesia (MgO) (*Magnesia Ponderosa*, B.P.). Both are sometimes spoken of as "calcined magnesia." A given weight of the official light magnesia occupies three and a half times the bulk of the same weight of heavy magnesia.

$$\begin{array}{ccccccc} 3MgCO_3, Mg2HO & = & 4MgO & + & H_2O & + & 3CO_2 \\ \text{Official Carbonate of magnesium.} & & \text{Oxide of magnesium.} & & \text{Water.} & & \text{Carbonic acid gas.} \end{array}$$

A trace only of magnesia is dissolved by water. Moisten grain or two of magnesia with water, and place the paste on a piece of red litmus-paper; the wet spot, after a time, becomes blue, showing that the magnesia is slightly soluble.

"*Effervescing Citrate of Magnesia*," so-called, is generally mixture of bicarbonate of sodium, citric acid, tartaric cid, sugar, either carbonate or sulphate of magnesium, or oth, and flavouring essences. True citrate of magnesium is asily made by combining together calcined magnesia and itric acid; it is frequently prescribed in France in doses of wo ounces.

The official Effervescing "Solution of Citrate of Magne- ium" (*Liquor Magnesii Citratis*, B.P.) is made by dissolving carbonate of magnesium in slight excess of solution of itric acid, adding lemon-syrup, placing the diluted liquid in n aërated-water bottle, dropping in crystals of bicarbonate of potassium, corking at once, "wiring," and shaking till the crystals are dissolved.

The formula of citrate of magnesium deposited from solution is $Mg_32C_6H_5O_7, 14H_2O$.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Add solution of hydrate or carbonate of ammonium to a magnesium solution (sulphate, for example), and warm the mixture in a test-tube; the precipitation of part only of the magnesium as (hydrate, $Mg2HO$, or carbonate, $MgCO_3$) occurs. Add now to a small portion of the mixture of precipitate and liquid a considerable excess of solution of chloride of ammonium; the precipitate is dissolved.

This is an important reaction, especially as regards carbonate of magnesium, the presence of chloride of ammonium enabling the analyst to throw out from a solution barium and calcium by an alkaline carbonate, magnesium being retained. The cause of this retention is found in the tendency of magnesium to form soluble double salts with potassium, sodium, or ammonium. In analysis, the chloride of ammonium should be added before the carbonate, as it is easier to prevent precipitation than to redissolve a precipitate once formed.

Second Analytical Reaction.—To some of the solution resulting from the last reaction, add solution of phosphate of sodium or ammonium; a white granular precipitate (phosphate of magnesium and ammonium, $MgNH_4PO_4$) results. ——*Third.* To another portion add arseniate of ammonium, a precipitate similar in appearance falls (arseniate of magnesium and ammonium, $MgNH_4AsO_4$).

Note.—Barium and calcium are also precipitated by alkaline phosphates and arseniates. The other precipitants of magnesium are also precipitants of barium and calcium. In other words, there is no *direct* test for magnesium. Hence the analyst always removes any barium or calcium by an alkaline carbonate, as above indicated; the phosphate of sodium (or arseniate or phosphate of ammonium) then becomes a very delicate test of the presence of magnesium. In speaking of magnesium tests, the absence of barium and calcium salts is to be understood.

QUESTIONS AND EXERCISES.

Name the natural sources of the various salts of magnesium.—Give a process for the preparation of Epsom salt.—Draw diagrams illustrative of the formation of sulphate of magnesium from *magnesite* and from *dolomite*.—Show by an equation the process for the preparation of the official Carbonate of Magnesium.—What circumstances determine the two different states of aggregation of the official Carbonates of Magnesium (*Magnesii Carbonas Ponderosa* and *Magnesii Carbonas Levis*, B.P) ?—What are the relations of *Magnesia Ponderosa*, B.P., and *Magnesia Levis*, B.P., to the official Carbonates of Magnesium ?—How much denser is the one than the other ?—Is magnesia soluble in water ?—How is "Fluid Magnesia" prepared ?—Mention the effects of heat and cold on "Fluid Magnesia."—Ascertain how much magnesia (MgO) can be obtained from 100 grains of Epsom salt.—Calculate the amount of official Carbonate of Magnesium which will yield 100 grains of magnesia.—Can magnesium be detected in presence of barium and calcium ?—Describe the analysis of an aqueous liquid containing salts of barium, calcium, and magnesium.—How may magnesium be precipitated from solutions containing ammoniacal salts ?

Quantivalence or Valency.

On reviewing the foregoing statements regarding compounds of the three univalent radicals—potassium, sodium, and ammonium, and the three bivalent elements—barium, calcium, and magnesium, the doctrine of quantivalence, or valency, will be more clearly understood and its usefulness be more apparent. Quantivalence, or the value of atoms, is, in short, in chemistry, closely allied to value in commercial barter. A number of articles, differing much in weight, appearance, and general characters, may be of equal money value; and if these be regarded, for convenience, as having a sort of unit of value, others worth double as much might be termed bivalent, three times as much trivalent, and so on. In like manner, chemical radicals, no matter whether elementary, like potassium (K), iodine (I), or sulphur (S), or compound, like those of nitrates (NO_3), sulphates (SO_4), or acetates ($C_2H_3O_2$), have a given chemical value in relation to each other, and are exchangeable for, or will unite with, each other to an extent determined by that value. Two such radicals may be considered to be present in a molecule of most ordinary salts, a basylous and an acidulous radical, one quantivalently balancing the other. The formulæ of the chief of these radicals and their quantivalence are given in the following Table. Examples of formulæ of salts containing univalent, bivalent, and trivalent radicals are given in the succeeding Table.

QUANTIVALENCE OF COMMON RADICALS.

Univalent Radicals, or *Monads*.		Bivalent Radicals, or *Dyads*.		Trivalent Radicals, or *Triads*.	
Acidulous.	Basylous.	Acidulous.	Basylous.	Acidulous.	Basylous.
H	H	O	Ca	PO_4	As
Cl	K	SO_4	Mg	BO_3	Sb
I	Na	CO_3	Zn	$C_6H_5O_7$	Bi
HO	NH_4	C_2O_4	Cu	AsO_3	Fe^{iii}(ic)
NO_3	Ag	$C_4H_4O_6$	Hg(ic)	AsO_4	or
$C_2H_3O_2$	Hg(ous)	S	Fe(ous)	$C_4H_3O_5$	Fe^{vi}_2(ic)

Note 1.—Hydrogen (H) as the basylous part of salts has entirely different functions to hydrogen (H) as the acidulous part. Acidulous hydrogen gives compounds commonly termed *hydrides* (*e.g.*, AsH_3); basylous hydrogen is the basylous radical of acids (*e.g.*, HCl, H_2SO_4). On the other hand, in compound radicals, *e.g.*, $C_2H_3O_2$, or NH_4, these properties of hydrogen are no longer apparent; the chemical force resident with the atoms of such radicals seems to be mainly exerted in binding those atoms together.

Note 2.—The name, symbol, quantivalence, and atomic weight of all the important elements are given in a Table immediately preceding the Index.

Examples of Formulæ of Salts containing Univalent, Bivalent, and Trivalent Radicals.

The reader will find instructive practice in writing twenty or thirty imaginary formulæ of salts by placing in juxtaposition acidulous and basylous radicals, as in the following Table of examples. Just as in a pair of scales a 2-lb. weight must be balanced by two 1-lb. weights, or a 4-lb. weight by two 2-lb. weights, or by one 3-lb. and one 1-lb. weight, so a bivalent radical unites with a bivalent radical or with two univalent radicals, a quadrivalent radical with two bivalent radicals, or with one trivalent and one univalent radical, and so on.

(R = any basylous radical.) (*R* = any acidulous radical.)

General formulæ.	*Examples.*
$\mathrm{R}'R'$	KI, $NaCl$, $NH_4C_2H_3O_2$, $AgNO_3$.
$\mathrm{R}''R'_2$	$CaCl_2$, $Zn2C_2H_3O_2$, $Pb2NO_3$ ($BaNO_3C_2H_3O_2$).
$\mathrm{R}'''R'_3$	$Bi3NO_3$, AsH_3, $SbCl_3$.
R'_2R''	K_2CO_3, Na_2SO_4, $H_2C_4H_4O_6$.
$\mathrm{R}'\mathrm{R}'R''$	$KHCO_3$, $NaHSO_4$, $KNaC_4H_4O_6$.
R'_3R'''	$(NH_4)_3PO_4$, $K_3C_6H_5O_7$, H_3AsO_3.
$\mathrm{R}'_2\mathrm{R}'R'''$	Na_2HPO_4, Na_2HAsO_4.
$\mathrm{R}''R''$	$CaCO_3$, MgO, $CuSO_4$, HgO, $FeSO_4$.
$\mathrm{R}''_3R'''_2$	Ca_32PO_4, $Ca_32C_6H_5O_7$.
$\mathrm{R}''\mathrm{R}'R'''$	$MgNH_4PO_4$, $CuHAsO_3$.
$\mathrm{R}'''R''R'$	$BiONO_3$.
$\mathrm{R}'''_2R''_2R''$	$Bi_2O_2CO_3$.
$\mathrm{R}'''_2R''_3$	As_2O_3, Sb_2O_3, Fe_2O_3, Fe_23SO_4.
$\mathrm{R}'''R'''$	$BiC_6H_5O_7$.
$\mathrm{R}'''_2R'_6$	Fe_2Cl_6, Fe_26NO_3, $Fe_26C_2H_3O_2$.

Quadrivalent Radicals or *Tetrads*, Quinquivalent Radicals or *Pentads*, and Sexivalent Radicals or *Hexads*, are known.

Cautions.—1. The student will not mistake valency for strength. Bivalent atoms, for example, will vary as much in *power* of chemical attachment as several two-armed boys will vary from each other in *power* of grasp. The greater the quantivalence of an atom, the more compounds it will form; the stability of those compounds is another affair altogether. Indeed, it often happens that the greater the complexity, the less the stability of a molecule. 2. A "radical" is a single or whole substance in a broad and general sense only, the great majority of radicals themselves admitting of subdivision. A molecule, like a crystal, is only broadly a whole or single thing, open to attack or cleavage from without, and probably then will split in more than one or two directions.

EXERCISE.

Write an exposition of the doctrine of Quantivalence within the limits of a sheet of note-paper.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION* OF A SALT OF **ONE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add yellow chromate of potassium to a portion of the solution to be examined; a precipitate indicates barium.

If no barium is present, add chloride and carbonate of ammonium, and boil; a precipitate indicates calcium.

If barium and calcium are proved to be absent, add chloride of ammonium, ammonia, and then either phosphate of sodium or arseniate of ammonium; a white granular precipitate indicates magnesium.

Ammonia is here added to yield the necessary elements to ammonio-magnesian phosphate or ammonio-magnesian arseniate, both of which are highly characteristic precipitates; and chloride of ammonium is added to prevent a mere partial precipitation of the magnesium by the ammonia.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF **ONE, TWO, OR ALL THREE** OF THE METALS, BARIUM, CALCIUM, MAGNESIUM.

Add chromate of potassium to the solution; barium, if present, is precipitated. Filter, if necessary, and add to the *filtrate* (that is, the liquid which has run through the filter) chloride, hydrate, and carbonate of ammonium, and boil; calcium, if present, is precipitated. Filter, if requisite, and add phosphate of sodium; magnesium, if present, is precipitated.

Note.—Red chromate of potassium must not be used in these operations, or a portion of the barium will remain in the liquid and be thrown down with, or in the place of, the carbonate of calcium (*vide* p. 113). The yellow chromate must not contain carbonate of potassium, or calcium will be precipitated with, or in the place of, barium. The absence of carbonate is proved by the non-occurrence of effervescence on the addition of hydrochloric acid to a little of the solution of the chromate, previously made hot in a test-tube. If the yellow chromate has been prepared by adding excess of ammonia to solution of red chromate of potassium, its addition to the liquid to be analysed must be preceded by that of solution of chloride of ammonium; the precipitation of a portion of the magnesium (by the free ammonia in the yellow chromate) is thus prevented—for solution of chloride of ammonium is a good solvent of hydrate (and carbonate) of magnesium, as already stated on page 134.

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* In preparing such solutions for analysis, salts should be selected which do not decompose each other. Chlorides will serve in most cases, but nitrates and acetates are still more convenient.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

To the solution add NH_4Cl, NH_4HO, $(NH_4)_2CO_3$; boil and filter.

<table>
<tr><td colspan="2">Precipitate
Ba Ca.
Wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4, and filter.</td><td colspan="2">Filtrate
Mg NH_4 Na K.
Add $(NH_4)_2HPO_4$, shake, filter.</td></tr>
<tr><td>Precipitate
Ba*</td><td>Filtrate
Ca.
Test by $(NH_4)_2C_2O_4$.</td><td>Precipitate
Mg.</td><td>Filtrate
NH_4 Na K.
Evap. to dryness, ignite, dissolve residue in water.
Test for K by Pt Cl_4.
" " Na " flame.
Test orig. sol. for NH_4.</td></tr>
</table>

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* It is perhaps scarcely necessary to state that this precipitate is not barium (Ba) itself but chromate of barium ($BaCrO_4$), as any reader who has carefully gone through the "foregoing analytical reactions" will know. Chemical symbols and formulæ are often used for mere shorthand purposes, but no intelligent student will thereby be misled. The occurrence of chromate of barium here, however, and under the circumstances described, is abundant evidence of the presence of barium (Ba, in some form or other) in the liquid analysed—which was a part of the problem to be solved by the operator. Similar remarks

Note 1.—The analysis of solutions containing the foregoing metals is commenced by the addition of chloride of ammonium (NH_4Cl) and ammonia (NH_4HO), simply as a precautionary measure, the former compound preventing partial precipitation of magnesium, the latter neutralizing acids. The carbonate of ammonium, $(NH_4)_2CO_3$, is the important group-reagent—the precipitant of barium and calcium.

Note 2.—In the above, and in subsequent charts of analytical processes, the leading precipitants will be found to be ammonium salts. These, being volatile, can be got rid of towards the end of the operations, and thus the detection of potassium and sodium be in no way prevented—an advantage which could not be had if such salts as chromate of potassium or phosphate of sodium were the group-precipitants employed.

Note 3.—Acetic, and not hydrochloric or nitric, acid is used in dissolving the barium and calcium carbonates, because chromate of barium—on the precipitation of which the detection of barium depends—is soluble in the stronger acids, and therefore could not be thrown down in their presence.

Note on Classification.—The compounds of barium, calcium, and magnesium, like those of the alkali metals, have many analogies; the carbonate, phosphate, and arseniate of each are insoluble in water, which sufficiently distinguishes them from the members of the class first studied. They possess, however, well-marked differences, so that their separation from each other is easy. The solubility of their hydrates in water marks their connection with *the alkali metals*; the slightness of that solubility, diminishing as we advance farther and farther from the alkalies, baryta being most and magnesia least soluble in water, points to their connection with the next class of metals, the hydrates of which are insoluble in water. These considerations must not, however, be over-valued. Though the solubility of their hydrates places barium nearest and magnesium farthest from the alkali metals, the solubility of their sulphates gives them the opposite order, magnesium sulphate being most soluble,

apply to the Ca, which is finally precipitated as oxalate (CaC_2O_4), to Mg, which is thrown out as ammonio-phosphate ($MgNH_4PO_4$), to NH_4, Na, and K, and to the elements similarly alluded to in the other subsequent Tables of "short" directions for analysis.

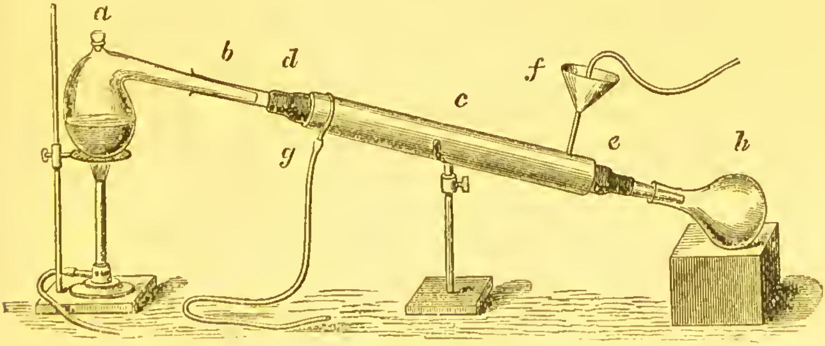
calcium sulphate next, strontium sulphate third (strontium is a rarer element, mentioned subsequently), while barium sulphate is insoluble in water. These elements are sometimes spoken of as *the metals of the alkaline earths.*

Note.—In connection with the bivalence of the atoms of Barium, Calcium, and Magnesium, it is interesting to note that just as bivalent acidulous radicals give salts containing two atoms of univalent basylous radicals, (K_2SO_4, H_2CO_3, $KNaC_4H_4O_6$), so bivalent basylous radicals yield salts containing two atoms of univalent acidulous radicals, as seen in acetonitrate of barium, $BaC_2H_3O_2NO_3$, a salt which is a definite compound, and not a mixture of acetate with nitrate. A large number of such salts is known.

Distillation.

The water with which, in analysis, solution of a salt or dilution of a liquid is effected should be pure. Well and river-waters are unfit for the purpose, because they contain alkaline and earthy salts (some 20 to 60 grains per gallon), derived from the soil through which the water percolates, and rain-water is not infrequently contaminated with the dust and *débris* which fall on the roofs whence it is usually collected. Such water is purified by *distillation*, an operation in which the water is, by ebullition, converted into steam, and the steam condensed again to water in a separate vessel, the fixed earthy and other salts remaining in the vessel in which the water is boiled. On the large scale, ebullition is effected in metal boilers having a hood or head in which is a wide lateral

Fig. 28.



DISTILLATION, ON A SMALL SCALE.

channel through which passes the steam; on the small scale, either a common glass flask is employed, into the neck of which, by a cork, is inserted a glass tube bent to an acute angle, or a *retort* is used (*a*, fig. 28), a sort of long-necked Florence flask, dexterously bent near the body by the glass-worker to an appropriate angle (hence the name *retort*, from *retorqueo*, I bend back). *Condensation* is effected by surrounding the lateral steam-tube with cold water. In large stills the steam-tube, or *condensing-worm*, is usually a metal (tin) pipe, twisted into a spiral form for the sake of compactness, and so fixed in a tub that a few inches of one end of the pipe may pass through and closely fit a hole bored near the bottom of the tub. Cold water is kept in contact with the exterior of the pipe, provision being made for a continuous supply to the bottom, while the lighter water, heated by the condensing steam, runs off from the top of the column. The condenser for a flask or retort may be a simple glass tube of any size, placed within a much wider tube (a common long, narrow lamp-glass answers very well for experimental operations), the inner tube being connected at the extremities of the wider by bored corks; a stream of water passes into one end of the enclosed space (the end farthest from the retort), through a small glass tube inserted in the cork, and out at the other end through a similar tube. The common (Liebig's) form of laboratory condenser is a glass tube three-fourths of an inch wide and a yard long (*b*, fig. 28), surrounded by a shorter tin or zinc tube (*c*, fig. 28) two inches in diameter, and having at each extremity a neck, through which the glass tube passes. The ends of the necks of the tin tube, and small portions of the glass tube near them, are connected by means of a strip of sheet caoutchouc carefully bound round, or by short, wide india-rubber tubes (*d* and *e*, fig. 28). An aperture (*f*, fig. 28) near the lower part of the tin tube provides for the admission of a current of cold water, by glass tubing or india-rubber tubing, from the house supply or from a vessel placed above the apparatus; and a similar aperture near the top (*g*, fig. 28) allows the escape of heated water into a vessel or sink. The inner tube may thus constantly be surrounded by cold water, and heated vapours passing through it be perfectly cooled and condensed—and collected in any receiver (*h*, fig. 28).

In distilling several gallons of water for analytical or medicinal purposes (*Aqua Destillata*, B.P.), the first two or three pints should be rejected, because they are likely to contain ammoniacal and other volatile impurities.

Water (*Aqua*, B.P.) is defined as "natural water, the purest that can be obtained, cleared, if necessary, by filtration; free from odour, unusual taste, and visible impurity. To be used whenever 'Water' is ordered in the British Pharmacopœia. In dispensing prescriptions, *aqua* should be understood to mean distilled water."

Rectification is the process of redistilling a distilled liquid. *Rectified spirit* is spirit of wine which has thus been treated.

Dry or *destructive distillation* is distillation in which the condensed products are directly formed by the decomposing influence of the heat applied to the dry or non-volatile substances in the retort or still.

Exercise.—Write from memory a short description of *distillation.*

RECAPITULATORY.

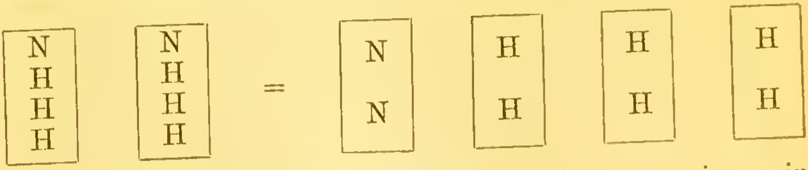
The subject just alluded to (distillation) naturally causes wonder respecting the cause of the physical differences between solid, liquid, and gaseous water. Common observation will have suggested to the student that the force of heat has much to do with the differences; and if he will turn to the chapter on *latent heat* in any Book on Physics, he will find that, as already indicated (p. 90), when ice liquefies by heat, a very large amount of heat must be given before the slightest rise of temperature occurs. Afterwards the addition of heat makes the water hotter and hotter, until one other point is reached (the boiling-point), when here again a great amount of heat is absorbed without causing the slightest rise in temperature. Afterwards more heat makes the gaseous water hotter and hotter, until, like a bar of iron, the steam, under special conditions, is made red-hot or even white-hot. Different bodies absorb different amounts of heat in changing their physical condition from solid to liquid, or liquid to gas (or vapour). The amount is constant for any one body; hence definite comparative numbers may be used for expressing the *latent heats* of substances.

The absorption of heat at particular (liquefying and vaporizing) points must not be confounded with an analogous physical action, namely, the absorption of heat which goes on when a body is rising in temperature. The amount of this absorption, also, differs with different substances. That is to say, if equal weights of several substances, all at the same temperature, be heated to a stated higher temperature, very different amounts of fuel will be required. The particular or specific amount in each case is always the same; hence the *specific heats* of substances may be expressed by numbers. See the chapter on "Specific Heat" in any manual of physics.

But after reading what has been stated respecting the constitution of matter (pp. 37 to 41), the chemical student will, in connection with the subject of distillation, be led, once more, to think over the subject of the molecular constitution of solid, liquid, and gaseous water, and of the molecular condition of bodies generally. As previously stated, little can be told him respecting the molecular condition of solids and liquids, for temperature and pressure affect them unequally; whence we conclude that though the relation to each other of the molecules of any one substance is constant, this relation is different in different bodies. Different *gases*, however, are not differently affected, but similarly affected, by temperature and pressure; whence we conclude that their molecular constitution—the relation of their molecules to one another—is similar.

Another gas, ammonia, has been brought before the reader since the molecular constitution of gases was considered.

A small quantity of ammonia gas enclosed in the upper part of a roughly graduated test-tube over *mercury* (*water* would dissolve it), and exposed to the continuous action of the electric spark, by means of wires of platinum fused in the sides of the tube, is decomposed into its elements, nitrogen and hydrogen, the bulk of gas operated on being exactly doubled. This expansion is not due to the gaseous molecules receding from each other, but to every two molecules becoming four similar-sized molecules:—



Here each space (rectangular chiefly for convenience in printing) represents a molecule, and each letter an atom. Each space, if regarded as the side of a double cube, may also, for the moment, represent two volumes, such two volumes yielding, in the decomposition, one volume of nitrogen and three volumes of hydrogen, or the four such double-cube volumes of ammonia shown in the diagram yielding two volumes of nitrogen and six volumes of hydrogen.

Remembering that a symbol (of a gas) represents one volume, and that *a formula (of a gas) always represents two volumes*, the pupil will now see how full of meaning is such an equation as the following, including, as it does, names of the elements, number of atoms, nature of the molecules, number of the molecules, weights of atoms of the molecules, and therefore weights of bulks of the bodies, or extent of expansion in the disunion of the elements, and therefore their extent of contraction in the act of union:—

$$2NH_3 = N_2 + 3H_2.$$

AT THIS STAGE THE LEARNER IS AGAIN RECOMMENDED TO READ THE PARAGRAPHS ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY (PAGES 29 TO 57), AND TO RETURN TO THEM FROM TIME TO TIME, UNTIL THEY ARE THOROUGHLY COMPREHENDED.

ZINC, ALUMINIUM, IRON.

These three elements are classed together for analytical convenience rather than for more general analogies.

ZINC.

Symbol, Zn. Atomic weight, 64·9.

Source.—Zinc is tolerably abundant in Nature as sulphide (ZnS) or *blende*, and carbonate ($ZnCO_3$) or *calamine* (from *calamus*, a reed, in allusion to the appearance of the mineral). The ores are roasted to expel sulphur, carbonic acid gas, and some impurities, and the resulting oxide heated with charcoal, when the metal vaporizes and readily condenses. Zinc is a brittle metal, but at a temperature somewhat below 300° F. is malleable, and may be rolled into thin sheets. Above 400° it is again brittle, and may then be pulverized. At 773° F. it melts, and at a bright red heat is volatile. Zinc in exceptionally fine powder ignites spontaneously, especially if damp, or if stored in a warm place.

Uses.—Its use as a metal is familiar; alloyed with nickel it yields german silver; with twice its weight of copper it forms common brass, and as a coating on iron (the so-called *galvanized* iron) greatly retards the formation of rust. Most of the salts of zinc are prepared, directly or indirectly, from the metal (*Zincum*, B.P.).

Quantivalence.—The atom of zinc is bivalent, Zn''.

Molecular Weight.—Some remarks on this point will be made under Mercury.

REACTIONS HAVING SYNTHETICAL INTEREST.

Sulphate of Zinc.

First Synthetical Reaction.—Heat zinc (4 parts) with water (20 parts) and sulphuric acid (3 fluid parts) in a test-tube (or larger vessel) until gas ceases to be evolved; solution of sulphate of zinc results. Filter (to separate the particles of lead, carbon, etc., present in common zinc) and concentrate the solution in an evaporating-dish; on cooling, colourless, prismatic crystals of Sulphate of Zinc ($ZnSO_4$, $7H_2O$) are deposited (*Zinci Sulphas*, B.P.).

$$\underset{\text{Zinc.}}{Zn_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\text{Sulphate of zinc.}}{2ZnSO_4} + \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Water.}}{xH_2O}$$

Ordinary zinc does not displace hydrogen from pure sulphuric acid alone, nor from pure water alone, yet it does from the mixture. The possible explanation is that as sulphuric acid combines with several different quantities of water to form definite hydrous compounds (H_2SO_4, H_2O; H_2SO_4,$2H_2O$; etc.), it is one or more of these that is decomposed with elimination of hydrogen. At present we can only say that an unknown (x) amount of water is required in the reaction.

Note.—This reaction affords hydrogen and sulphate of zinc; it also develops electricity. Of several methods of evolving hydrogen, it is the most convenient; of the two or three means of preparing sulphate of zinc, it is that most commonly employed; and of the many reactions which may be utilized in the development of voltaic electricity, it is one of the most convenient. The apparatus in which the reaction is effected differs according to the requirements of the operator: if the sulphate of zinc alone is wanted, an open dish is all that is necessary, the action being, perhaps, accelerated by heat; if hydrogen, a closed vessel and delivery-tube; if electricity, certain vessels called cells, and various complementary materials, forming altogether what is termed a battery. In each operation for one of the three the other two are commonly wasted. It would not be difficult for the operator, as a matter of amusement, to construct an apparatus from which all three should be collected.

Purification.—Impure sulphate of zinc may be purified in the same manner as impure chloride (*see* next Reaction).

Sulphate of zinc is isomorphous with sulphate of magnesium, and, like that salt, loses six-sevenths of its water of crystallization at 212° F.

Chloride of Zinc.

Second Synthetical Reaction.—Digest zinc in hydrochloric acid mixed with half its bulk of water; the resulting solution contains chloride of zinc. Evaporate the liquid till no more steam escapes; Chloride of Zinc ($ZnCl_2$) in a state of fusion remains, and, on cooling, is obtained as an opaque white solid (*Zinci Chloridum*, B.P.). It is soluble in water or alcohol.

$$\underset{\text{Zinc.}}{Zn_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Chloride of zinc.}}{2ZnCl_2} + \underset{\text{Hydrogen.}}{2H_2}$$

This reaction is analogous to that previously described. The process and product are those of the British Pharmacopœia. Burnett's deodorizing or disinfecting liquid is solution of chloride of zinc.

Purification of Chloride or Sulphate of Zinc.—Zinc sometimes contains traces of iron or lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts: they may be recognised in the liquids by applying the test described hereafter (p. 151) to a little of the solution in a test-tube. Should either be present in the above solution, a little chlorine water is added to the liquid till the odour of chlorine is permanent, and then the whole well shaken with some hydrate of zinc or the common official "carbonate" of zinc (really hydrato-carbonate: *see* next page). In this way iron is precipitated as ferric hydrate, and lead as peroxide:—

$$\underset{\text{Ferrous chloride.}}{*2FeCl_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ferric chloride.}}{*Fe_2Cl_6}$$

$$\underset{\text{Ferric chloride.}}{Fe_2Cl_6} + \underset{\text{Hydrate of zinc.}}{3ZnH_2O_2} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Chloride of zinc.}}{3ZnCl_2}$$

$$\underset{\text{Chloride of lead.}}{PbCl_2} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Hydrate of zinc.}}{2ZnH_2O_2} = \underset{\text{Peroxide of lead.}}{PbO_2} + \underset{\text{Chloride of zinc.}}{2ZnCl_2} + \underset{\text{Water.}}{2H_2O}$$

In the British Pharmacopœia, the possible presence of impurities in the zinc is recognised, and the process of purification just described incorporated with the process of preparation of *Zinci Chloridum*, *Liquor Zinci Chloridi*, and *Zinci Sulphas.* In the purification of the sulphate of zinc, the action of chlorine on any ferrous sulphate will result in the formation of ferric sulphate as well as ferric chloride:—

$$6FeSO_4 + 3Cl_2 = 2\,(Fe_2 3SO_4) + Fe_2Cl_6\,;$$

carbonate of zinc will then give chloride as well as sulphate of zinc, and thus the whole quantity of sulphate of zinc be slightly contaminated by chloride. On evaporating and crystallizing, however, the chloride of zinc will be retained in the mother-liquor. These processes of purification admit of *general* application.

For Liquor Zinci Chloridi, B.P., 1 pound of zinc is placed in a mixture of 44 fluid ounces of hydrochloric acid and 20 of water, the mixture ultimately warmed until no more gas escapes, filtered into a bottle, chlorine water added until the liquid, after shaking, smells fairly of chlorine, about half an ounce or somewhat more of carbonate of zinc shaken up with the solution until a brown precipitate (of ferric hydrate, or peroxide of lead, or both) appears, the whole filtered, and the filtrate evaporated to 40 fluid ounces. One fluid ounce contains 366 grains of chloride of zinc. If, on testing a little of the solution first produced with ammonia and sulphydrate of ammonium, the precipitate is quite white, neither iron nor lead was present in the zinc, and the treatment with chlorine water and carbonate of zinc is to be omitted.

Carbonate of Zinc.

Third Synthetical Reaction.—To solution of any given quantity of sulphate of zinc in twice its weight of water (in a test-tube, evaporating basin, or other large or small vessel) add about an equal quantity of carbonate of sodium, also dissolved in twice its weight of water, and boil; the resulting white precipitate is so-called Carbonate of Zinc (*Zinci Carbonas*, B.P.), a compound of carbonate ($ZnCO_3$) and hydrate ($Zn2HO$), in the proportion of one molecule of the former and two of the latter, together with a molecule of water (H_2O). It may be washed, drained, and dried in the usual manner. It is used in the arts under the name of *zinc-white*.

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* It will be noticed that the atom of iron is represented, in these equations, as exerting both bivalent and trivalent activity; this will be alluded to when iron comes under consideration.

$$\underset{\text{Sulphate of zinc.}}{3ZnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonate of sodium.}}{3Na_2CO_3} = \underset{\text{Official carbonate of zinc.}}{ZnCO_3,\ 2ZnH_2O_2} + \underset{\text{Carbonic acid gas.}}{2CO_2} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4}$$

Calamina Præparata, B.P., is a smooth, pale pinkish-brown powder, obtained by calcining and powdering native carbonate of zinc or *calamine*, and freeing the product from gritty particles by elutriation. *Prepared calamine* is chiefly carbonate of zinc with some oxide of iron, etc.

Elutriation (*Lat. elutriatus ; elutrio ; eluo ;* I wash out). This fractional operation consists in straining off water (or other liquids—light like ether, or heavy like chloroform) containing lighter particles in suspension from heavier and coarser particles which have become deposited. The decanted fluid yields a sediment of the fine particles on standing. By allowing a varying number of seconds to elapse between the shaking and the decantation, and by the use of fluids of different specific gravities and different degrees of limpidity or viscidity, substances of different specific gravities or particles of different degrees of fineness of any one substance, may be separated from each other.

Acetate of Zinc.

Fourth Synthetical Reaction.—Collect on a filter the precipitate obtained in the last reaction, wash with distilled water, and dissolve a portion in strong acetic acid; the resulting solution contains acetate of zinc, and, on evaporating and setting aside, yields lamellar pearly crystals ($Zn2C_2H_3O_2,\ 2H_2O$), *Zinci Acetas*, B.P.

$$\underset{\text{Official carbonate of zinc.}}{ZnCO_3,2ZnH_2O_2} + \underset{\text{Acetic acid.}}{6HC_2H_3O_2} = \underset{\text{Acetate of zinc.}}{3(Zn2C_2H_3O_2)} + \underset{\text{Water.}}{5H_2O} + CO_2$$

Oxide of Zinc.

Fifth Synthetical Reaction.—Dry the remainder of the precipitated carbonate (by placing the open filter on a plate over a dish of water kept boiling), and then heat it in a small crucible till trial samples taken out of the crucible from time to time cease to effervesce on the addition of water and acid; the product is Oxide of Zinc (*Zinci Oxidum*, B.P.), much used in the form of Ointment (*Unguentum Zinci*, B.P.).

$$\underset{\text{Official carbonate of zinc.}}{ZnCO_3, 2ZnH_2O_2} = \underset{\text{Oxide of zinc.}}{3ZnO} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Note.—This oxide is yellow while hot, and of a very pale yellow or slight buff tint when cold, not actually white like the oxide prepared by the combustion of zinc in air. The preparation of the latter variety, which also occurs in commerce, can only be practically accomplished on the large scale; but the chief features of the action may be observed by heating a piece of zinc on charcoal in the blowpipe-flame (fig. 29) till it burns; flocks escape, float about in the air, and slowly fall. These are the old *Flores Zinci*, *Lana Philosophica*, or *Nihilum Album*.

Fig. 29.

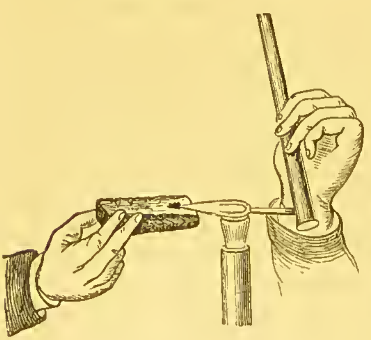
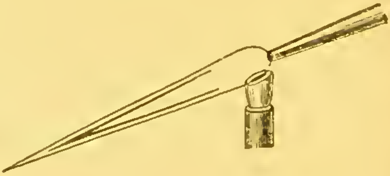


Fig. 30.



THE BLOWPIPE.

A clear blowpipe-flame consists more or less of two portions (*see* fig. 30), an inner cone, at the apex of which are hot hydrocarbon gases greedy of oxygen, and an outer cone at the apex of which is excess of hot oxygen. At the latter point oxidizable metals, etc., are readily oxidized, as in the foregoing experiment, and that part of the flame is therefore termed *the oxidizing flame;* in the inner flame oxides and other compounds (a grain of acetate of lead may be employed for illustration) are reduced to the metallic state, hence that part is termed *the reducing flame.* A blowpipe-flame is much altered in character by slight variations in the position of the nozzle of the blowpipe, by the form of the nozzle, by the force with which air is expelled from the blowpipe, and by the character of the jet of gas.

Oxide of zinc slowly absorbs carbonic acid from moist air, and is partly reconverted into the hydrato-carbonate.

Valerianate of Zinc.

Sixth Synthetical Reaction.—The Valerianate of Zinc ($Zn2C_5H_9O_2,H_2O$), *Zinci Valerianas*, B.P., is prepared by mixing strong solutions of sulphate of zinc and valerianate of sodium, cooling, separating the white pearly crystalline substance, evaporating at 200° F. to a low bulk, cooling, again separating the lamellar crystals, washing the whole product with a small quantity of cold distilled water, draining and drying by exposure to air at ordinary temperatures. Valerianate of zinc is soluble in ether, alcohol, or hot water.

$$\underset{\text{Sulphate of zinc.}}{ZnSO_4} + \underset{\text{Valerianate of sodium.}}{2NaC_5H_9O_2} = \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Valerianate of zinc.}}{Zn2C_5H_9O_2}$$

Note.—The compounds of zinc described in the foregoing six reactions are the only ones mentioned in the British Pharmacopœia: the processes are also those of that work. *Sulphide* and *Hydrate of Zinc* are mentioned in the following analytical paragraphs. The formula of *Sulphite of Zinc* is $ZnSO_3, 3H_2O$.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—To solution of a zinc salt (sulphate, *e.g.*), in a test-tube, add solution of sulphydrate of ammonium (NH_4HS); a white precipitate (sulphide of zinc, ZnS) falls, insoluble in acetic, soluble in the stronger acids.

Note.—This is the only white sulphide that will be met with. Its formation, on the addition of the sulphydrate of ammonium, is therefore highly characteristic of zinc. If the zinc salt contains iron or lead as impurities, the precipitate will have a dark appearance, the sulphides of those metals being black. Hydrate of aluminium, which is also white and precipitated by sulphydrate of ammonium, is the only substance for which sulphide of zinc is likely to be mistaken, and *vice versâ;* but, as will be seen immediately, there are good means of distinguishing these from each other.

Second Analytical Reaction.—To solution of a zinc salt add ammonia; a white precipitate (hydrate of zinc, Zn2HO) appears. Add excess of ammonia; the precipitate is redissolved. This reaction at once distinguishes a zinc salt from an aluminium salt, hydrate of aluminium being insoluble in diluted ammonia.

Other Analytical Reactions.—The fixed alkali-hydrates afford a similar reaction to that just mentioned, the hydrate of zinc redissolving if the alkali is free from carbonate. Carbonate of ammonium yields a white precipitate of carbonate and hydrate, soluble in excess. The fixed alkaline carbonates give a similar precipitate, which is not redissolved if the mixed solution and precipitate be well boiled. Ferrocyanide of potassium precipitates white ferrocyanide of zinc (Zn_2FeCy_6).

Sulphate of magnesium, which is isomorphous with and sometimes indistinguishable in appearance from sulphate of zinc, is not precipitated from its solutions either by ferrocyanide of potassium or sulphydrate of ammonium.

Antidotes.—There are no efficient chemical means of counteracting the poisonous effects of zinc. Large doses, fortunately, act as powerful emetics. If vomiting has not occurred, or apparently to an insufficient extent, solution of carbonate of sodium (common washing soda), immediately followed by white of egg and demulcents, may be administered, and then the stomach be cleared.

QUESTIONS AND EXERCISES.

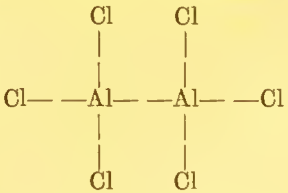
Give the sources and uses of metallic zinc.—Give a diagram of the action of zinc on diluted sulphuric acid.—How may solutions of Chloride or Sulphate of Zinc be purified from salts of iron? Give equations for the reactions.—State the formula of the official Carbonate of Zinc, and illustrate by a diagram the reaction which takes place in its production. —Give an equation for the synthesis of Acetate of Zinc.—In what respect does Oxide of Zinc, resulting from the ignition of the carbonate, differ from that produced during the combustion of the metal?—How is Valerianate of Zinc prepared?—What are the properties of Valerianate of Zinc?—Name the more important tests for zinc.—How would you distinguish, chemically, between solutions of Sulphate of Zinc and Alum?—Describe the treatment in cases of poisoning by zinc salts.—Give reactions distinguishing Sulphate of Zinc from Sulphate of Magnesium.

ALUMINIUM.

Symbol, Al. Atomic weight, 27.

Note.—In the formulæ of aluminium salts, it will be observed that to one atom of metal there are three atoms of other univalent radicals; hence, apparently, the atom of aluminium is trivalent, Al'''. But possibly it is quadrivalent; for one molecule of aluminium compounds includes two atoms of the metal, three-fourths only of whose power may be supposed to be exerted in retaining the other constituents of the molecule, the remaining fourth enabling the aluminium atoms themselves to keep together. This is graphically shown in the following formula of chloride of aluminium (Al_2Cl_6), which represents each aluminium atom as a body having four arms or bonds, three of which are engaged in grasping the arms of univalent chlorine atoms, while the fourth grasps the corresponding arm of its brother aluminium atom. Such *structural formulæ* or *graphic formulæ*, as they are called, are useful in facilitating the acquirement of hypotheses regarding the constitution of chemical substances, especially if the error be avoided of supposing that they are pictures either of the position or absolute power of atoms in a molecule, or, indeed, the true representation of a molecule at all; for on this point man knows little or nothing. $AlCl_3$ may be the formula at *very* high temperatures.

Chloride of Aluminium.



Source.—Aluminium is abundant in Nature, chiefly as silicate in clays, slate, marl, granite, basalt, and a large number of minerals. *Mica* or *talc* consists chiefly of silicates of aluminium, iron, magnesium, and potassium. The sapphire and ruby are almost pure oxide of aluminium. *Rotten stone* is a soft, friable, aluminium silicate containing a little organic matter.

The metal aluminium is obtained from the double chloride of aluminium and sodium by the action of metallic sodium, the source of the chloride being the mineral *bauxite*, a more or less ferruginous hydrate of aluminium; also by electrolysis. It is readily attacked by inorganic and organic acids.

Aluminium readily alloys with other metals. One part fused with nine of copper gives *aluminium bronze*. *Aluminium-steel* is a hard and tenacious alloy of a little aluminium with the iron.

Alum (*Alumen*, B.P.), a double sulphate of aluminium and ammonium ($Al_2 3SO_4, Am_2SO_4, 24H_2O$), or of aluminium and potassium ($Al_2 3SO_4, K_2SO_4, 24H_2O$), may be obtained from aluminous schist (from σχιστός, *schistos*, divided), a sort of pyritous slate or shale, by exposure to air; oxidation and chemical change produce sulphate of aluminium, sulphate of iron, and silica, from the silicate of aluminium and bisulphide of iron (iron pyrites) originally present in the shale. The sulphate of aluminium and sulphate of iron are dissolved out of the mass by water, and sulphate or chloride either of ammonium or of potassium added; on concentrating the liquid, alum crystallizes out, while the more soluble iron salt remains in the mother-liquor.

It is more frequently prepared by directly decomposing the silicate of aluminium in the calcined shale of the coal-measures by hot sulphuric acid, ammonium or potassium salts being added from time to time, until a solution strong enough to crystallize is obtained. The liquid, well agitated during cooling, deposits alum in minute crystals termed *alum-flour*, which is afterwards recrystallized.

Alums.—There are several *alums*, iron or chromium taking the place of aluminium, and potassium or sodium that of ammonium, all crystallizing in an eight-sided form, the octahedron—a sort of double pyramid. They are, apparently, alike in chemical constitution, and their general formula (M = either metal) is $M'''_2 3SO_4$, M'_2SO_4, $24H_2O$. The alum of the manufacturer commonly occurs in colourless, transparent, octahedral crystals, massed in lumps, which are roughly broken up for trade purposes, but still exhibit the faces of octahedra. It contains sulphate of ammonium or sulphate of potassium, according as one or other is the cheaper. At the present time potassium alum is the variety met with in trade.

Note on Constitution or Structure.—In presence of the fact that a great change in the properties of sulphate of aluminium, sulphate of potassium, and water, ensues when those three substances unite to form alum, it would seem to be wrong to picture alum by a formula still reflecting those three substances, thus $Al_23SO_4,K_2SO_4,24H_2O$. Many chemists admit this, and find reasonable excuse in sheer inability to offer any more probable formula in the present stage of chemical knowledge. Many chemists, on the other hand, defend the formula, and explain that while no doubt the particles in each of the original separate substances are united by *atomic* or ordinary chemical attraction or affinity, those substances are, in alum, united by *molecular* chemical attraction. But this view involves the assumption of the existence of either a new force or of two forms of chemical force, in which case the old position that permanent and entire alterations in properties are due to the action of a single force, the chemical force, is no longer tenable. It is to be feared that both learner and teacher must be content to remain for the present in somewhat of a dilemma. The discovery that resolves this dilemma will probably lay bare the cause of the properties and phenomena attendant upon the formation of all salts containing what is termed "water of crystallization," as well as of "double salts," "solutions," "alloys," "amalgams," and perhaps upon what is conveniently spoken of as "the variations in the valency of atoms."

Preparation of Alum.—Prepare alum by heating a small quantity of powdered pipeclay (silicate of aluminium) with about twice its weight of sulphuric acid for some time, dissolving out the resulting sulphate of aluminium and excess of sulphuric acid by water, and adding carbonate of potassium to the clear filtered solution until, after well stirring, the excess of acid is neutralized. (If too much carbonate be added, the hydrate of aluminium precipitated when the carbonate is first poured in will not be redissolved on well mixing the whole. Perhaps the readiest indication of neutrality in this and similar cases is the presence of *a little* precipitate after stirring and warming the mixture.) On evaporating the clear solution, crystals of alum are obtained.

Sulphate of Aluminium or "*Alum-cake*" ($Al_23SO_4,9H_2O$) prepared from natural silicates in the manner just described, is a common article of trade, serving most of the manufacturing purposes for which alum was formerly employed.

Dried alum (*Alumen Exsiccatum*, B.P.) is potassium alum from which the water of crystallization has been expelled by heat, the temperature not exceeding 400° F. By calculation from the molecular weight of alum, it will be found that the salt contains between 47 and 48 per cent. of water. At temperatures above 400° F. ammonium alum is decomposed, sulphate of ammonium and sulphuric anhydride escaping, and pure oxide of aluminium (Al_2O_3) remaining. Dried alum rapidly reabsorbs water from the atmosphere, and is slowly but completely soluble in water.

Roche alum, or *Rock alum* (*roche*, French, rock), is the name of an impure native variety of alum containing iron. The article sold under this name is generally an artificial mixture of common alum with oxide of iron.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—To a solution of an aluminium salt (alum, for example, which contains sulphate of aluminium) add sulphydrate of ammonium (NH_4HS); a gelatinous white precipitate (hydrate of aluminium) falls:—

$$Al_23SO_4 + 6NH_4HS + 6H_2O = Al_26HO + 3(NH_4)_2SO_4 + 6H_2S.$$

Second Analytical Reaction.—To solution of alum add ammonia, NH_4HO; hydrate of aluminium falls: add excess of ammonia; the precipitate is, practically, insoluble.

Principle of Dyeing by help of Mordants.—The precipitated hydrate of aluminium, alumina, has great affinity for vegetable colouring-matters, and also for the fibre of cloth. Once more perform the above experiment, but before adding the ammonia introduce some decoction of logwood, solution of cochineal, or other similar-coloured liquid, into the test-tube. Add now the ammonia, and set the tube aside for the alumina to fall; the latter takes down with it all the colouring principle. In dye works, the fabrics are passed through liquids holding the alumina but weakly in solution, and then through the colouring solutions; from the first bath the fibres abstract alumina, and from the second the alumina abstracts colouring matter. Some other metallic hydrates, notably those of tin and iron, resemble alumina in this property; they are termed *mordants* (from *mordens*, biting); the substances they form with colouring-matters have the name of *lakes*.

Third Analytical Reaction.—To the solution of alum add solution of potash; again hydrate of aluminium falls. Add excess of potash, and agitate; the precipitate dissolves.

Hydrate of aluminium may be precipitated from this solution by neutralizing the potash with hydrochloric acid, and adding ammonia, until, after shaking, the mixture has an ammoniacal smell, or by adding solution of chloride of ammonium to the potash liquid. But the former way is the better; for it is difficult to know when a sufficiency of the chloride of ammonium has been poured in; whereas reaction with blue and red litmus-paper at once enables the operator to know when excess of hydrochloric acid or of ammonia has been added.

Alkaline carbonates, phosphates, arseniates, and salts of other acidulous radicals also decompose solutions of aluminium salts and produce insoluble compounds of that metal with the several acidulous radicals (except the carbonic), but the resulting precipitates are of no special interest.

QUESTIONS AND EXERCISES.

What is there remarkable about the quantivalence of aluminium?—Practically what is the quantivalence of the atom of aluminium?—Enumerate the chief natural compounds of aluminium?—Write down a formula which will represent either of the alums.—Which alum is official, and commonly employed in the arts?—State the source and explain the formation of alum.—What is the crystalline form of alum? Work a sum showing how much dried alum is theoretically producible from 100 pounds of alum. *Ans.*, 52 lb. 6 oz.—Show by figures how ordinary ammonium alum is capable of yielding 11·356 per cent. of oxide of aluminium.—Why are aluminium compounds used in dyeing?—How are salts of aluminium analytically distinguished from those of zinc?

IRON.

Symbol, Fe. Atomic weight, 56.

Sources.—Compounds of iron are abundant in Nature. *Magnetic Iron Ore*, or *Loadstone* (*Lodestone* or *Leadstone*, from the Saxon *lædan*, to lead, in allusion to its use, or rather, to the use of magnets made from it, in navigation), is the chief ore from which Swedish iron is made; it is a compound of ferrous and ferric oxide (FeO, Fe_2O_3). Much of the Russian iron is made from *Specular Iron Ore* (from *speculum*, a mirror, in allusion to the lustrous nature of the crystals of this mineral); this and *Red Hæmatite* (from αἷμα, *haima*, blood, so named from the colour of its streak), an ore raised in Lancashire, are composed of ferric oxide only (Fe_2O_3). *Brown Hæmatite*, an oxyhydrate, is the source of much of the French iron. *Spathic Iron Ore* (from *spatha*, a slice, in allusion to the lamellar structure of the ore) is a ferrous carbonate ($FeCO_3$). An impure ferrous carbonate forms the *Clay Ironstone*, whence most of the English iron is derived. The chief Scotch ore is also an impure carbonate, containing much bituminous matter: it is known as *Black Band*. *Iron Pyrites* (from πῦρ, *pur*, fire, in allusion to the production of sparks when sharply struck) (FeS_2) is a yellow, lustrous mineral of use only for its sulphur. As met with in coal, it is commonly termed *coal brasses*. Ferrous carbonate ($FeCO_3$), chloride ($FeCl_2, 4H_2O$), and sulphate ($FeSO_4, 7H_2O$) sometimes occur in springs, the water of which is hence termed *chalybeate* (*chalybs*, steel).

Process.—Iron is obtained from its ores by processes of roasting, and reduction of the resulting impure oxide with coal or charcoal in the presence of chalk, the latter uniting with tho sand, clay, etc., to form a fusible slag. The *cast iron* thus produced may bo converted into *wrought iron* by burning out the 4 or 5 per cent. of carbon, silicon, and other impurities present, by oxidation in a furnaco—the old operation termed *puddling*. *Steel* is iron containing from one to two per cent. of carbon, and is made by the now celebrated Bessemer process of burning out from cast iron the variable amount of carbon it contains, and then adding melted iron containing a known proportion of carbon. The official variety of tho metal (*Ferrum*, B.P.) is "annealed iron wire, having a diametor about 0·005 of an inch (about No. 35 wiro gauge), or wrought-iron nails; freo from oxide": those being the forms in which iron is conveniently employed for conversion into its compounds. In the form of a fine powder (*see* the 17th Reaction) metallic iron is employed as a medicine.

Properties.—The specific gravity of pure iron is 7·844; of the best bar iron 7·7. Its colour is bluish white or grey. Bar iron requires the highest heat of a wind-furnace for fusion, but below that temperature assumes a pasty consistence, and in that state two pieces may be joined or *welded* (Germ. *wellen*, to join) by the pressure of blows from a hammer. A little sand thrown upon the hot metal facilitates this operation by forming with the superficial oxide of iron a fusible slag, which is dispersed by the blows: the purely metallic surfaces are thus better enabled to come into thorough contact and enter into perfect union. Iron is highly ductile, and of all common metals possesses the greatest amount of tenacity. At a high temperature it burns in the air, forming red oxide of iron. Ordinary *iron rust* is chiefly red oxide of iron, with a little ferrous oxide and carbonate; it is produced by action of the moist carbonic acid of the air and subsequent oxidation. Steam passed over scrap iron heated to redness gives hydrogen gas and black oxide of iron.

Quantivalence.—Iron combines with other elements and radicals in two proportions; those salts in which the atom of iron appears to possess inferior affinities (in which the other radicals are in the less amount) are termed *ferrous*, the higher being *ferric* salts. In the former the atom exerts bivalent (Fe'' or Fe_2^{iv}), in the latter trivalent activity (Fe''' or Fe_2^{vi}) as seen in the formulæ of the chlorides, $FeCl_2$ (possibly Fe_2Cl_4) and Fe_2Cl_6 (perhaps $FeCl_3$ at *very* high temperatures). The atom of iron is also sometimes considered to be sexivalent, on account of the analogy of its compounds with those of chromium, which is sexivalent, if the formula of its fluoride (CrF_6) be correct, and because the composition of *ferrate of potassium* (K_2FeO_4), a deep-purple salt (obtained on warming a mixture, in a test-tube, of a few fragments of solid hydrate of potassium and of perchloride of iron with a few drops of bromine), is best explained on the assumption of the sexivalence of its iron.

Why the quantivalence of such atoms as that of iron should vary is not at present known.

The Nomenclature of Iron Salts.—For educational and descriptive purposes, also, the two classes of compounds are very conveniently spoken of as *ferrous* and *ferric*, the syllable "*ferr*," common to all, indicating their allied ferruginous character, the syllables *ous* and *ic* indicating the lower and higher class respectively—functions fulfilled by these two syllables in other similar cases (sulphurous and sulphuric, mercurous and mercuric). Officially the iron salts are known by other names, thus, *Sulphate of Iron* (*Ferri Sulphas*) and *Phosphate of Iron* (*Ferri Phosphas*), names which are chemically inexplicit, for there are two sulphates and two phosphates, and the terms do not define which salt is intended. Consistency and uniformity would demand that the names Ferrous Sulphate, Ferrous Phosphate, or similar terms, should be employed. Practically, however, the old names cause no confusion, inasmuch as only one sulphate, phosphate, etc., are used in medicine; moreover, the higher salts usually have the prefix *per* attached (as persulphate, perchloride). These names are already well known, can easily be rendered in Latin, and then admit of simple abbreviations and adaptations such as are employed in prescriptions, advantages not possessed by the more rational terms. While, therefore, the comprehension of the chemistry of iron is rendered simple and intelligible by the use of the terms ferrous and ferric, the employment of older and less definite names may very well be continued in pharmacy as being practically more convenient.

Reactions having Synthetical Interest.

FERROUS SALTS.

Green Sulphate of Iron. Ferrous Sulphate.

First Synthetical Reaction.—Place iron (small tacks) in sulphuric acid diluted with eight times its bulk of water (in a test-tube, basin, or other vessel of any required size), accelerating the action by heat until effervescence ceases.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Water.}}{xH_2O} = \underset{\text{Ferrous sulphate.}}{2FeSO_4} + \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Water.}}{xH_2O}$$

The solution contains what is generally known as Sulphate of Iron, that is, Ferrous Sulphate, the lower of the two sulphates, and will yield crystals of that substance ($FeSO_4, 7H_2O$) (*Ferri Sulphas*, B.P.) on cooling or on further evaporation; or if the hot concentrated solution be poured into alcohol, the mixture being well stirred, the sulphate is at once thrown down in minute crystals (*Ferri Sulphas Granulata*, B.P.). At a temperature of 212° F. ferrous sulphate loses six-sevenths of its water, and becomes the *Ferri Sulphas Exsiccata*, B.P. (For the nature of the chemical action with iron and diluted sulphuric acid, *see* the analogous zinc Reaction on p. 146.)

Other Sources of Ferrous Sulphate.—In the laboratory, ferrous sulphate is often obtained as a by-product in making sulphuretted hydrogen.

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

In manufactories it occurs as a by-product in the decomposition of aluminous shale, as already noticed (p. 154).

Ten grains of granulated sulphate of iron dissolved in one ounce of water constitutes "Solution of Sulphate of Iron," B.P. "The solution should be recently prepared," because of its liability to absorb oxygen and become spoilt through formation of ferric oxysulphate (see below).

Notes.—Ferrous sulphate is sometimes termed *green vitriol.* Vitriol (from *vitrum*, glass) was originally the name of any transparent crystalline substance: it was afterwards restricted to the sulphates of zinc, iron, and copper, which were, and still are, occasionally known as white, green, and blue vitriol. *Copperas* (probably originally *Copper-rust*, a term applied to verdigris and other green incrustations of copper) is another name for this sulphate of iron, sometimes distinguished as *green copperas*, sulphate of copper being blue copperas. Solid sulphate of iron is a constituent of *Pilula Aloes et Ferri*, B.P. Ferrous sulphate forms a light green double salt with sulphate of ammonium ($FeSO_4, Am_2SO_4, 6H_2O$). ($Am = NH_4$.)

Ferrous sulphate, when exposed to the air, gradually turns brown through absorption of oxygen, ferric oxysulphate (Fe_2O2SO_4) being formed. The latter is not completely dissolved by water, owing to the formation of a still lower insoluble oxysalt ($Fe_4O_5SO_4$) and the soluble ferric sulphate; $5(Fe_2O2SO_4) = Fe_4O_5SO_4 + 3(Fe_23SO_4)$.

Iron heated with undiluted sulphuric acid gives sulphurous acid gas and ferrous sulphate:—

$$Fe_2 + 4H_2SO_4 = 2SO_2 + 2FeSO_4 + 4H_2O.$$

Carbonate of Iron. Ferrous Carbonate.

Second Synthetical Reaction.—To solution of ferrous sulphate, boiling, in a test-tube, add a solution of carbonate of ammonium, $(NH_4)_2CO_3$, in recently boiled hot water; a white precipitate of ferrous carbonate ($FeCO_3$) is thrown down, rapidly becoming light-green, bluish-green, and, after a long time, red, through absorption of oxygen, evolution of carbonic acid gas, and formation of ferric oxyhydrate.

$$\underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Carbonate of ammonium.}}{(NH_4)_2CO_3} = \underset{\text{Ferrous carbonate.}}{FeCO_3} + \underset{\text{Sulphate of ammonium.}}{(NH_4)_2SO_4}$$

Saccharated Carbonate of Iron.—The above precipitate, rapidly washed with hot well-boiled distilled water, and the moist powder mixed with sugar and quickly dried—in short, all possible precautions taken to avoid exposure to air—forms the Saccharated Carbonate of Iron (*Ferri Carbonas Saccharata*, B.P.).

The official proportions are two ounces of the sulphate and one ounce and a quarter of the carbonate, each dissolved in half a gallon of hot water. The solutions are mixed and set aside in a deep, well-covered pan, the supernatant liquid poured off when the precipitate has subsided, the pan again filled up with boiling water, the liquid once more poured away, the precipitate transferred to a calico filter, drained, gently pressed, and, while still somewhat moist, rubbed in a mortar with one ounce of sugar, and finally dried over a water-bath. Saccharated Carbonate of Iron, mixed with a fourth of its weight of Confection of Roses, forms the *Pilula Ferri Carbonatis*, B.P.

Notes.—The red powder formerly termed Carbonate or Subcarbonate of Iron (*Ferri Carbonas* or *Ferri Subcarbonas*) was ferrous carbonate washed and dried with free exposure to air, the product thus, by the absorption of oxygen and the elements of water and elimination of carbonic acid gas, becoming ferric oxyhydrate, a compound which will come under notice subsequently (pp. 169 and 171). Ferrous carbonate is said to be more easily dissolved in the stomach than any other iron preparation. It is so unstable and prone to oxidation, that it must be washed in water containing no dissolved air and mixed with the sugar (which protects it from oxidation) as quickly as possible. In making the official compound mixture of iron (*Mistura Ferri Composita*, B.P.), "Griffith's mixture," the prepared ingredients, including the carbonate of potassium, should be placed in a bottle of the required size, space being left for the crystals or solution of ferrous sulphate, which should be added last, the bottle immediately filled up with the rose-water and securely corked; the minimum of oxidation is thus ensured. Two molecular weights of the carbonate of potassium to one of the sulphate of iron are ordered in the official mixture; hence, as the ferrous carbonate decomposes, the carbonic acid produced does not necessarily escape, but converts carbonate into bicarbonate of potassium. *Pilula Ferri*, B.P., *Iron Pill* or "Blaud's Pill," is also prepared with sulphate of iron and carbonate of potassium.

$$FeSO_4 + K_2CO_3 = FeCO_3 + K_2SO_4.$$

Arseniate of Iron. Ferrous Arseniate.

Third Synthetical Reaction, by which the lower arseniate of iron, ferrous arseniate (*Ferri Arsenias*, B.P.) (Fe_32AsO_4), partially oxidized, is formed. This will be noticed again under Arsenium.

Phosphate of Iron. Ferrous Phosphate.

Fourth Synthetical Reaction.—To a hot solution of ferrous ulphate in a test-tube add a hot solution of phosphate of odium, and a little of a solution of bicarbonate of sodium; he lower phosphate of iron, ferrous phosphate (Fe_32PO_4), s precipitated (*Ferri Phosphas*, B.P.).

$$\underset{\text{Ferrous sulphate.}}{3FeSO_4} + \underset{\text{Phosphate of sodium.}}{2Na_2HPO_4} + \underset{\text{Bicarbonate of sodium.}}{2NaHCO_3} =$$

$$\underset{\text{errous phosphate.}}{Fe_32PO_4} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Officially, solutions of 3 ounces of sulphate of iron in 30 of ot water, and 2¾ of phosphate in 30 of hot water, together ith ¾ of an ounce of bicarbonate of sodium dissolved in little water, are well mixed, filtered, the precipitate well ashed with hot water, and, to prevent oxidation as much as possible, dried at a temperature not exceeding 120° F. These proportions will be found to fairly accord with the molecular weights of the crystalline salts, multiplied as indicated in the above equation. $3(FeSO_4, 7H_2O)=834$: $2(Na_2HPO_4, 12H_2O)=716$; $2(NaHCO_3)=168$. This reaction also occurs in making *Syrupus Ferri Phosphatis*, B.P.

The use of the bicarbonate of sodium is to ensure the absence of free sulphuric acid in the solution. Sulphuric acid is a powerful solvent of ferrous phosphate. It is impossible to prevent the separation of sulphuric acid, if only the 834 parts of ferrous sulphate and 716 parts of phosphate of sodium be employed. Ferrous phosphate is white, but soon oxidizes and becomes slate-blue. The official salt should contain at least 47 per cent. of hydrous ferrous phosphate, $Fe_3(PO_4)_2, 8H_2O$, with ferric phosphate and some oxide.

Sulphide of Iron. Ferrous Sulphide.

Fifth Synthetical Reaction.—In a gas-flame or spirit-flame strongly heat sulphur with about twice its weight of iron filings in a test-tube (or in an earthen crucible in a furnace); ferrous sulphide (FeS) is formed. When cold, add water to a small portion, and then a few drops of sulphuric acid; sulphuretted hydrogen gas (H_2S), known by its odour, is evolved. $FeS+H_2SO_4=FeSO_4+H_2S$.

Sticks of sulphur pressed against a white-hot bar of cast iron give a pure form of ferrous sulphide. The liquid sulphide thus formed is allowed to drop into a vessel of water (Sulphide of Iron, B.P.). Or melted sulphur may be poured into a crucible full of red-hot iron nails, when a quantity of fluid ferrous sulphide is at once formed and may be poured out on a slab.

Green Iodide of Iron. Ferrous Iodide.

Sixth Synthetical Reaction.—Place a piece of iodine, about the size of a pea, in a test-tube, with a small quantity of water, and add a few iron filings, small nails or iron wire. On gently warming, or merely shaking if longer time be allowed, the iodine disappears and, on filtering, a clear light-green solution of iodide of iron (FeI_2) is obtained. On evaporation, the solid iodide remains.

Solid iodide of iron contains about 18 per cent. of water of crystallization and a little oxide of iron. It is deliquescent and liable to absorb oxygen from the air with formation of insoluble ferric oxyiodide or hydrato-iodide. Iodide of iron thus spoilt may be purified by re-solution in water, addition of a little more iodine and some iron, warming, filtering, and evaporating as before. Syrup of iodide of iron which has become brown may usually be restored by immersing the bottle in a water-bath and slowly warming.

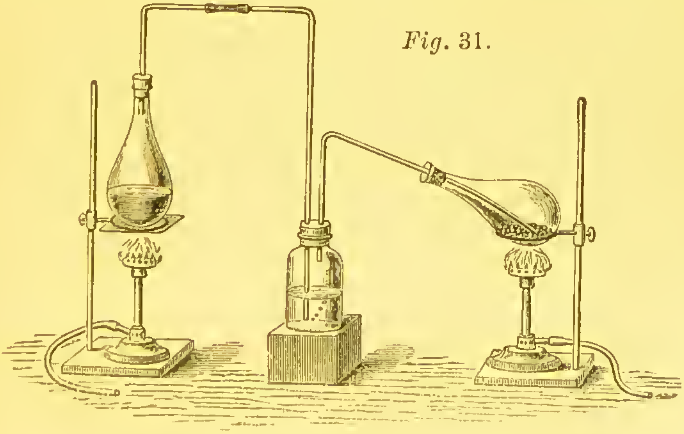
Ferrous Bromide ($FeBr_2$), occasionally used in medicine, could be made, as might be expected, in the same way as the iodide.

FERRIC SALTS, ETC.

Anhydrous Perchloride of Iron. Ferric Chloride.

Seventh Synthetical Reaction.—Pass chlorine (generated from black oxide of manganese and hydrochloric acid in a flask) through strong sulphuric acid contained in a small bottle, and thence by the ordinary narrow glass tubing quite to the bottom of a test-tube containing twenty or thirty small iron tacks (or a Florence flask containing 2 or 3 ounces—*see* fig. 31), the latter kept hot by a gas-flame; the higher chloride

Fig. 31.



PREPARATION OF ANHYDROUS FERRIC CHLORIDE.

of iron, ferric chloride, or the perchloride* of iron (Fe_2Cl_6) is formed and condenses in the upper part of the tube or flask as a mass of small, dark, iridescent crystals. When a tolerably thick crust of the salt is formed, break off the part of the glass containing it, being careful that the remaining corroded tacks are excluded, and place it in ten or twenty times its weight of water; the resulting solution, poured off from any pieces of glass, is a pure neutral solution of ferric chloride, and will be serviceable for analytical reactions.

Precaution.—The above experiment must be conducted in the open air, or in a cupboard having a draught outwards.

Anhydrous Ferrous Chloride.—In breaking up the vessel, scaly crystals of this substance ($FeCl_2$), of a light-buff colour, will be observed adhering to the nails.

Note.—Solution of ferric chloride evolves some hydrochloric acid on boiling, while a darker-coloured solution of ferric oxychloride remains.

Formula of Ferric Chloride.—Qualitative analysis shows that ferric chloride contains iron and chlorine. Quantitative analysis shows that to 56 parts of iron there are 106·5 parts of chlorine; total 162·5. And as 56 parts of iron are indicated by the symbol Fe, and 106·5 of chlorine by the symbol and figure Cl_3, the formula for ferric chloride will, *so far*, be $FeCl_3$. But equal volumes of gases and vapours contain equal numbers of molecules (see p. 52). A volume which, if water vapour, weighs 18 grains will, if ammonia, weigh 17 grains; or, if carbonic acid gas, 44 grains; and, if perchloride of iron vapour, 325 grains. And as these respective volumes contain equal numbers of molecules, one molecule of each will be represented by the same figures respectively. That is to say, the equal volumes differing in weight as the figures 18, 17, 44 and 325 differ, and the volumes containing equal numbers of molecules, the respective molecules themselves will differ in weight as the figures 18, 17, 44 and 325 differ. The formula H_2O represents the 18 parts of water, or one molecule; NH_3, the 17 of ammonia, or one molecule; CO_2, the 44 of carbonic acid gas, or one molecule; and the 325 parts by weight of perchloride of iron can only be represented by the formula Fe_2Cl_6; for $FeCl_3$ would only represent half the number thus obtained by actual experiment. Hence Fe_2Cl_6 is the formula for a molecule of perchloride of iron and not $FeCl_3$—at all events at the temperatures of the experiments (320° to 440° C.).

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* The prefix *per* (and *hyper*) used here and elsewhere is from ὑπέρ, *hyper*, over or above, and simply means the "highest" of several. Thus perchloride, the highest *chloride*.

Green Chloride of Iron. Hydrous Ferrous Chloride. Solution of Hydrous Ferric Chloride.

Eighth Synthetical Reaction.—Dissolve iron tacks or wire, in a test-tube, in hydrochloric acid; hydrogen escapes, and the solution on cooling, or on evaporation and cooling, deposits *crystallized ferrous chloride*, containing four molecules of water of crystallization ($FeCl_2$, $4H_2O$). A syrup of ferrous chloride is official (*Syrupus Ferri Subchloridi*, B.P.).

Through a portion of the solution of ferrous chloride pass chlorine gas; the ferrous chloride becomes *ferric chloride.*

The excess of chlorine dissolved by the liquid in this experiment may be removed by ebullition; but the ferric chloride is liable to be slightly decomposed. The free chlorine is better carried off by passing a current of air through the liquid for some time.

Hydrous Ferric Chloride. (*The Official Process.*)

Ninth Synthetical Reaction.—To another portion of the solution of ferrous chloride, in a test-tube, add a little hydrochloric acid; heat the liquid, and continue to drop in nitric acid until the black colour it first produces disappears; the resulting reddish-brown liquid is solution of ferric chloride.

$$\underset{\text{Ferrous chloride.}}{6FeCl_2} + \underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Ferric chloride.}}{3Fe_2Cl_6} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The black substance is a compound of nitric oxide gas (NO) with some ferrous salt: it is decomposed by heat.

This is the process for producing the *Liquor Ferri Perchloridi Fortior*, B.P., 4 ounces of iron wire, 20½ fluid ounces of hydrochloric acid, 1½ of nitric acid, and sufficient water being employed, and the product boiled down to 17½ fluid ounces. Practically it is impossible so to apportion the acids that a solution shall result containing neither excess of acid nor of metal, nor contain ferric nitrate. For most medicinal purposes, however, solution of perchloride of iron containing hydrochloric acid is said to be unobjectionable. On the large scale some time may be saved by adopting the official plan of adding the acid solution of ferrous chloride to the nitric acid.

Diluted to four times its bulk by water, this strong solution gives the *Liquor Ferri Perchloridi*, B.P.,—or 1 volume with 1 of spirit, and sufficient water to produce 4 volumes, gives the *Tinctura Ferri Perchloridi*, B.P.

Note.—The spirit in the latter preparation is unnecessary, useless, and deleterious; for it acts neither as a special solvent nor as a preservative—the offices usually performed by alcohol (*Tincturæ et Succi*, B.P.)—but, unless the liquid contain excess of acid, decomposes the ferric chloride and causes the formation of an insoluble oxychloride of iron. Even if the tincture be acid, it slowly loses colour, ferrous chloride and chlorinetted ethereal bodies being formed. The *Liquor*, which is similar in strength, is doubtless destined to displace the tincture altogether.

Solution of Ferric Chloride evaporated yields a mass of yellow crystals composed of Fe_2Cl_6 $12H_2O$, or, rarely, red crystals, having the formula Fe_2Cl_6 $5H_2O$.

Persulphate of Iron. Ferric Sulphate.

Tenth Synthetical Reaction.—Dissolve about three-quarters of an ounce of ferrous sulphate and a sixth of its weight of sulphuric acid in an ounce and a half of water in an evaporating dish, heating the mixture and dropping in nitric acid until the black colour it first produces disappears. The resulting liquid, when made of a certain prescribed strength, is the solution of ferric sulphate, or higher sulphate, "Solution of Persulphate of Iron" of the British Pharmacopœia, a heavy, dark-red liquid.

$$\underset{\text{Ferrous sulphate.}}{6FeSO_4} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Ferric sulphate.}}{3(Fe_23SO_4)} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The black colour, as in the previous reaction, is due to a compound of ferrous salt with nitric oxide ($2FeSO_4 + NO$).

The definite official solution of ferric sulphate (*Liquor Ferri Persulphatis*, B.P.) is made by adding 6 fluid drachms of sulphuric acid to half a pint of water, warming, dissolving 8 ounces of crystals of sulphate of iron in the liquid, then pouring it into nitric acid (6 fluid drachms or rather more) slightly diluted, until the mixture turns to a reddish colour, and ruddy nitrous vapours cease to be produced. The whole should measure 11 fluid ounces, being diluted or further evaporated, as the case may be, to this bulk.

Note.—In reactions in which iron passes from ferrous to ferric condition it assumes different properties; the atoms of the metal, as we believe, passing from bivalent to trivalent activity.

Ferric Oxyhydrate, or Hydrated Oxide of Iron.

Eleventh Synthetical Reaction.—Pour a portion of the solution of ferric sulphate into excess of solution of soda; moist *ferric hydrate*, $Fe_2 6HO$, is precipitated. Wash the precipitate by decantation or on a filter, and dry it on a plate over boiling water; *ferric oxyhydrate*, $Fe_2O_2(HO)_2$, (*Ferri Peroxidum Hydratum*, B.P.) remains. When rubbed to a fine powder, it is fit for medicinal use.

$$\underset{\text{Ferric sulphate.}}{Fe_2 3SO_4} + \underset{\text{Soda.}}{6NaHO} = \underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4}$$

$$\underset{\text{Ferric hydrate.}}{Fe_2 6HO} = \underset{\text{Ferric oxyhydrate.}}{Fe_2O_2 2HO} + \underset{\text{Water.}}{2H_2O}$$

Either of the other alkalies (potash or ammonia) will produce a similar reaction; but soda is cheapest.

Ferric hydrate is an antidote to arsenic if administered directly after the poison has been taken. It converts the soluble arsenic (As_2O_3) into insoluble ferrous arseniate:—

$$2(Fe_2 6HO) + As_2O_3 = Fe_3 2AsO_4 + 5H_2O + Fe2HO.$$

Dried ferric hydrate (then become an oxyhydrate, $Fe_2O_2 2HO$) has less action on arsenic. Even the moist recently prepared hydrate ($Fe_2 6HO$) loses much of this power as soon as it has become converted into an oxyhydrate ($Fe_4O_3 6HO$), a change which occurs though the hydrate be kept under water (W. Procter, jun.). According to T. and H. Smith, this decomposition occurs gradually, but in an increasing ratio; so that after four months the power of the moist mass is reduced to one-half, and after five months to one-fourth. Now the mere loss of water is not usually followed by any alteration of the essential chemical properties of a compound. It would seem, therefore, that ferric hydrate (two molecules) ($Fe_4 12HO$) probably suffers, on standing, actual decomposition into oxyhydrate ($Fe_4O_3 6HO$) and water ($3H_2O$), and does not merely lose water already existing in it as water. Ferric hydrate is also far more readily soluble in hydrochloric acid, tartaric acid, citric acid, and acid tartrate of potassium, than ferric oxyhydrate. Any formulæ exhibiting ferric hydrate ($Fe_2 6HO$) as a combination of ferric oxide and water (Fe_2O_3, $3H_2O$), or the oxyhydrate ($Fe_2O_2 2HO$), as a similar combination (Fe_2O_3, H_2O), are apparently, for these and other reasons, scarcely correct.

Peroxide of Iron. Ferric Oxide.

The above oxyhydrate, $Fe_2O_2 2HO$, sometimes shortly termed *peroxide of iron* (B.P.), further decomposes when heated to low redness, ferric oxide or true peroxide of iron (Fe_2O_3) remaining.

$$Fe_2O_2 2HO = Fe_2O_3 + H_2O.$$

The six univalent atoms of the HO (hydroxyl), the characteristic elements of all hydrates, are thus, by two successive steps, split up into water and oxygen. But between the hydrate and oxide there obviously may be another oxyhydrate in which only 2HO is displaced by O″; and such a compound is well known; it is a variety of brown iron ore. The other oxyhydrate, $Fe_2O_2 2HO$, is also native (needle iron ore), as well as being the *Ferri Peroxidum Hydratum*, B.P.

"Ferri Peroxidum Humidum"	$Fe'''_2 \; 6HO$
A variety of brown iron ore	$Fe'''_2O'' \; 4HO$
"Ferri Peroxidum Hydratum" (needle ore)	$Fe'''_2O''_2 \; 2HO$
Ferric Oxide	$Fe'''_2O''_3$

The moist ferric hydrate, as already stated, when kept for some months, even under water, loses the elements of water, and is converted into an oxyhydrate, having the formula $Fe_4H_6O_9$ (limonite or brown hæmatite), which is either a compound of the above oxyhydrates ($Fe_2O 4HO + Fe_2O_2 2HO$), or is a definite intermediate oxyhydrate ($Fe_4O_3 6HO$).

By ebullition with water for seven or eight hours, ferric hydrate is decomposed into water, and an oxyhydrate having the formula $Fe_4H_2O_7$ (Saint-Gilles), which is either a mixture of the official oxyhydrate (Fe_2O_22HO) with ferric oxide (Fe_2O_3) or a definite intermediate body (Fe_4O_52HO). The relation of these bodies to each other will be apparent from the following Table, in which, for convenience, the formulæ of ferric hydrate and oxide are doubled :—

Ferric hydrate (and as stalactite) . . .	$Fe_4\ 12HO$
Kilbride mineral (?)	Fe_4O10HO
Brown iron ore (Huttenrode and Raschau)	$Fe_4\ O_28HO$
Old, or frozen, ferric hydrate (and limonite)	$Fe_4\ O_36HO$
Ferric oxyhydrate (B.P.) (and gothite) . .	$Fe_4\ O_44HO$
Boiled ferric hydrate (and turgite) . . .	$Fe_4\ O_52HO$
Ferric oxide (red hæmatite, etc.)	$Fe_4\ O_6$

A ferric oxycarbhydrate (Fe_4OCO_38HO) has been obtained.

The official ferric oxyhydrate (Fe_2O_22HO) was formerly made by mixing solutions of ferrous sulphate and carbonate of sodium and exposing the resulting ferrous carbonate to the air until it was nearly all converted into ferric oxyhydrate; hence its old name, still sometimes seen on shop bottles, of *Ferri Carbonas* and *Ferri Subcarbonas*. Possibly it sometimes contained a little of the oxycarbhydrate just mentioned.

Ferric Oxide. (*Another Process.*)

Twelfth Synthetical Reaction.—Roast a crystal or two of ferrous sulphate (mixed with a little sulphur to aid the reduction) in a small crucible until fumes cease to be evolved; the residue is a variety of ferric oxide (Fe_2O_3), or peroxide of iron, known in trade as *red oxide of iron*, *colcothar*, *crocus*, *rouge* (mineral), *Venetian red*, etc. It has sometimes been used in pharmacy in mistake for the official oxyhydrates (*vide* 11th Synthetical Reaction), from which it differs not only in composition but in the important respect of being almost insoluble in acids.

Acetate of Iron. Ferric Acetate.

Thirteenth Synthetical Reaction.—Digest recently washed and drained ferric hydrate in glacial acetic acid; ferric acetate, $Fe_2 6C_2H_3O_2$, is produced.

$$\underset{\text{Ferric hydrate.}}{Fe_2 6HO} + \underset{\text{Acetic acid.}}{6HC_2H_3O_2} = \underset{\text{Ferric acetate.}}{Fe_2 6C_2H_3O_2} + \underset{\text{Water.}}{6H_2O}$$

When the ferric hydrate of this reaction is prepared from five fluid parts of the official solution of persulphate of iron (p. 169), and is dissolved in three fluid parts of liquefied glacial acetic acid, the whole being diluted with water to ten fluid parts, the product is *Liquor Ferri Acetatis Fortior*, B.P. One fluid part of this Strong Solution of Acetate of Iron diluted with water to four fluid parts gives the official Solution of Acetate of Iron, *Liquor Ferri Acetatis*, B.P. Five fluid parts of the strong solution, one of acetic acid, five of rectified spirit, and sufficient water to produce twenty fluid parts, give the *Tinctura Ferri Acetatis*, B.P.

The "Scale" Compounds of Iron.

Fourteenth Synthetical Reaction.—Repeat the eleventh reaction, introducing a little solution of citric or tartaric acid or acid tartrate of potassium, before adding to the alkali (soda, potash, or ammonia), and notice that now no precipitation of ferric hydrate occurs. This experiment serves to illustrate not the manufacture of a scale compound, but the chemistry of the manufacture. The effect is due to the formation of double compounds, termed Ammonio-Citrate, Potassio-Citrate, Ammonio-Tartrate, Potassio-Tartrate, and similar sodium compounds of Iron, which remain in solution along with the secondary product—sulphate of the alkali metal. Such ferric compounds, made with certain prescribed proportions of recently prepared ferric hydrate (from which all alkaline sulphate has been washed), and the respective acids (tartaric or citric) or acid salts (acid tartrate of potassium), etc., and the solutions evaporated to a syrupy consistence and spread on smooth plates to dry, form the scale preparations known as *Ferri et Ammonii Citras*, B.P., and *Ferri Potassio-tartras*, or rather, *Ferrum Tartaratum*, B.P. A mixture of ferric citrate with citrate of ammonium and citrate of quinine yields, by similar treatment, the well-known scales of *Ferri et Quininæ Citras*, B.P.

Specimens of these substances may be prepared by attending to the following details. It is essential, first, that the ferric hydrate be thoroughly washed, or an insoluble oxysulphate will be formed; secondly, that the ferric hydrate be rapidly washed, or an insoluble ferric oxyhydrate will be produced; thirdly, that the whole operation be conducted quickly, or reduction to green ferrous salt will occur; fourthly, that the solutions of the salts be not evaporated at a higher temperature than that stated, or decomposition will take place; and, fifthly, that excess of ferric hydrate be employed.

In the pharmacopœial process for the three-scale compounds, the ferric hydrate is in each case freshly made from solution of ferric sulphate by precipitation with solution of ammonia:—

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{Fe_2 3SO_4} + \underset{\substack{\text{Hydrate of}\\\text{ammonium.}}}{6NH_4HO} = \underset{\substack{\text{Ferric}\\\text{hydrate.}}}{Fe_2 6HO} + \underset{\substack{\text{Sulphate of}\\\text{ammonium.}}}{3\,(NH_4)_2SO_4}$$

the solution of ferric sulphate being made of a definite strength from a known weight of ferrous sulphate. The reason for adopting this course is, that ferric hydrate is unstable and cannot be weighed, because it cannot be dried without decomposing and becoming insoluble, as explained under the 11th Reaction. This definite solution of ferric sulphate (*Liquor Ferri Persulphatis*, B.P.) is made as already described (*see* p. 169).

Ferri et Ammonii Citras, B.P.—Ferric hydrate is dissolved in solution of citric acid, ammonia added, and the whole evaporated to dryness.

To prepare the ferric hydrate, dilute ten fluid ounces of the above solution of ferric sulphate with about a quart of water; pour this into two or three pints of water containing excess of solution of ammonia—about eight fluid ounces of "Strong Solution of Ammonia," or twenty-four ounces of "Solution of Ammonia." (If the opposite course were adopted—the alkaline liquid poured into the ferric solution—the precipitate would contain ferric oxysulphate, or hydrato-sulphate, which interferes with the brilliancy of the scales.) Thoroughly stir the mixture (it will smell strongly of ammonia if enough of the latter has been used), allow the precipitate to subside, pour away the supernatant liquid, add more water, and repeat the washing until a little of the liquid tested for by-product (sulphate of ammonium) by solution of chloride or nitrate of barium ceases to give a white precipitate (sulphate of barium). Collect the ferric hydrate on a filter, drain, and add it, while still moist, to a solution of four ounces of citric acid in four of water, placed in an evaporating-basin over a water-bath; stir frequently, until nearly the whole of the hydrate has dissolved, or until the acid is fully saturated with the hydrate and some of the latter remains insoluble. To the mixture, when cold, add nearly two fluid ounces of strongest (or five and a half of weak) solution of ammonia, filter, evaporate over a water-bath to the consistence of syrup, thinly spread on panes of glass, and dry (at a temperature not exceeding 100° F.). The product scales off the glass in deep-red transparent laminæ.

Ferri et Quininæ Citras, B.P.—Ferric hydrate and pure quinine are dissolved in solution of citric acid, ammonia added, and the whole evaporated to dryness. The product contains citrate of iron, citrate of quinine, and citrate of ammonium.

The ferric hydrate is obtained from four and a half fluid ounces of the solution of ferric sulphate, with all the precautions described in the previous paragraph, a proportionate quantity of ammonia being employed.

While the ferric hydrate is being washed, prepare the quinine by dissolving one ounce of the ordinary sulphate of quinine in eight ounces of distilled water, acidified with sufficient sulphuric acid to dissolve the sulphate (about twelve fluid drachms of the official "diluted sulphuric acid"), and to the clear liquid add solution of ammonia, well mixing the product by stirring, until the whole of the quinine is precipitated (that is, until the mixture, after thorough agitation, smells of ammonia). Collect the precipitate on a filter, let it drain, and wash away adhering solution of sulphate of ammonium by passing through it about a pint and a half of distilled water.

(It will be observed that the principle involved in the preparation of quinine from its sulphate is identical with that which obtains in the precipitation of alumina, ferric hydrate, or hydrate of zinc, etc. Such a soluble sulphate—or, indeed, any similar soluble salt—has its acidulous constituent removed by the superior affinity of the basylous radical in ammonia, or other alkali, an insoluble precipitate and a new soluble sulphate being formed. The latter is washed away, leaving the former pure. In such manipulations, when economy has to be practised, soda is the alkali generally employed. Ammonia, however, has the advantage of showing the moment when its work of removing an acidulous radical is completed; for the salts which ammonium forms with such acidulous radicals as those represented by the formulæ SO_4, Cl, NO_3, and $C_2H_3O_2$ are inodorous, while ammonia has a powerful odour; so long, therefore, as the salt to be decomposed is not wholly attacked, the addition of ammonia does not give an ammoniacal odour to the mixture, the ammonia, as such, being, in fact, destroyed; but when the work is accomplished, the quantity of ammonia last added remains as ammonia, and communicates its natural smell to the liquid.)

The ferric hydrate and quinine being now washed and drained, dissolve the former, and afterwards the latter, in a solution of three ounces of citric acid in five of distilled water, the acid liquid being warmed over a water-bath, and portions of the precipitates stirred in as fast as solution is effected. "Let the solution cool, then add, in small quantities at a time, twelve fluid drachms of solution of ammonia diluted with two fluid ounces of distilled water, stirring the solution briskly, and allowing the quinine which separates with each addition of ammonia to dissolve (in the acid) before the next addition is made (excess of ammonia must be avoided, or the quinine will be precipitated). Filter the solution, evaporate to the consistence of a thin syrup, and then dry in thin layers on flat porcelain or glass plates at a temperature of 100° F. Remove the dry salt in flakes, and keep it in a stoppered bottle."

Ferrum Tartaratum, B.P. (*Ferri et Potassii Tartras*, U.S.P.).—Ferric hydrate is dissolved in solution of acid tartrate of potassium, and the whole evaporated to dryness.

The ferric hydrate obtainable from six fluid ounces of the official solution of ferric sulphate by the action of ammonia, in the manner detailed in the previous paragraphs, is mixed (in a mortar), while still moist but well drained, with two ounces of acid tartrate of potassium. The whole is set aside for about twenty-four hours, occasionally triturated to promote contact and reaction of the molecules (otherwise somewhat sluggish in attacking each other), and then heated in a dish over a water-bath to a temperature not exceeding 140° F.; a pint of distilled water is then added, and the mixture kept warm until nothing more will dissolve;

filtered, evaporated at a temperature not exceeding 140° F. (greater heat causes decomposition), and, when the mixture has the consistence of syrup, spread on panes of glass and allowed to dry (in any warm and open place shown by a thermometer to be not much hotter than 100° F.). The dry salt is thus obtained in flakes. It should be kept in well-closed bottles.

The foregoing are the only official scale preparations of iron. Many others of similar character might be formed. The *Citrate* dissolves slowly in cold but readily in warm water. Few crystallize or give other indications of definite chemical composition. Their properties are only constant so long as they are made with unvarying proportions of constituents. Want of chemical compactness, the loose state in which the iron is combined, precludes their recognition as well-defined chemical compounds, yet possibly enables them to be more readily assimilated as medicines than some of the more definite ferrous and ferric salts. A definite *ferrous tartrate* ($FeC_4H_4O_6$) and *ferrous citrate* ($FeHC_6H_5O_7$, H_2O) have been obtained by reaction of iron and acid in hot water. They occur as white gritty masses of microscopic crystals. A *sodio-ferrous citrate* ($FeNaC_6H_5O_7$) and *hydrato-citrate* ($FeNa_2HOC_6H_5O_7$) may be obtained in scales. In the United States Pharmacopœia *Ferri et Ammonii Tartras* is included. *Ferric phosphate* ($Fe_2 2PO_4$), when freshly precipitated, is soluble in solutions of citrates of the alkali-metals, and the mixtures on evaporation on glass plates yield scales.

Wine of iron, or "Steel" wine (*Vinum Ferri*, B.P.), made by digesting iron wire in sherry wine, probably contains a little tartrate of potassium and iron and other iron salts, formed by action of the metal on the small quantities of acid tartrate of potassium and tartaric, citric, malic and acetic acids present in the wine. *Vinum Ferri Citratis*, B.P., is a solution of ammonio-citrate of iron in orange wine.

Pernitrate of Iron. Ferric Nitrate.

Fifteenth Synthetical Reaction.—Place a few iron tacks in dilute nitric acid and set aside; solution of ferric nitrate, or pernitrate of iron, is formed ($Fe_2 6NO_3$).

$$\underset{\text{Iron.}}{Fe_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Ferric nitrate.}}{Fe_2 6NO_3} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitric oxide.}}{2NO}$$

This solution, made with care and of a prescribed strength, forms the *Liquor Ferri Pernitratis*, B.P. The process is as follows:—Four and a half fluid ounces of nitric acid are diluted with sixteen ounces of distilled water, and one ounce of iron wire, free from rust, dissolved in the mixture, the latter being kept cool to avoid violence of action. The liquid is finally filtered and diluted to thirty fluid ounces.

Ferric nitrate and ferric acetate unite to form various acetonitrates, amongst which is one having the formula $Fe_2(C_2H_3O_2)_4NO_3HO, 4H_2O$, crystallizing in hard, shining brownish-red prisms.

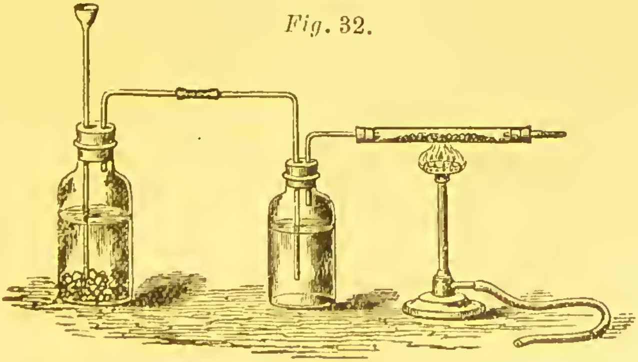
Reduced Iron.

Sixteenth Synthetical Reaction.—Pass hydrogen gas (dried by passing over pieces of chloride of calcium contained in a tube, or through sulphuric acid in a wash-bottle) over a small quantity of ferric oxyhydrate contained in a tube arranged horizontally (a test-tube the bottom of which has been accidentally broken serves very well), the oxyhydrate being kept hot by a gas-flame; oxygen is removed by the hydrogen, steam escapes at the open end of the tube, and after a short time, when moisture ceases to be evolved, metallic iron, in a minute state of division, remains. (*See* fig. 32.)

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{Fe_2} + \underset{\text{Water.}}{3H_2O}$$

While still hot, throw the iron out into the air; it takes fire and falls to the ground as oxide.

Fig. 32.



PREPARATION OF REDUCED IRON.

If the ferric oxide is reduced in an iron tube heated by a strong furnace, the particles of iron aggregate to some extent, and, when cold, are only slowly oxidized in dry air. This latter form of reduced iron is *Fer réduit*, or, *Quevenne's Iron*, the *Ferri pulvis, or Ferrum Redactum*, B.P.—"a fine greyish-black powder, strongly attracted by the magnet, and exhibiting metallic streaks when rubbed with firm pressure in a mortar." It is often administered in the form of lozenges (*Trochisci Ferri Redacti*, B.P.), gum and sugar protecting the iron from oxidation as well as forming a vehicle for its administration.

Note 1.—The spontaneous ignition of the iron in the above experiment is an illustration of the influence of minute division on chemical affinity. The action is the same as occurs whenever iron rusts, and the heat evolved and the amount of oxide formed are not greater from a given quantity of iron; but the surface exposed to the action of the oxygen of the air is, in the case of this variety of reduced iron, so enormous compared with the weight of the iron, that heat cannot be conducted away sufficiently fast to prevent elevation of temperature to a point at which the whole becomes incandescent. In the slow rusting of iron, escape of heat occurs, but is not observed, because spread over a length of time: in the spontaneous ignition of reduced iron, the whole is evolved at one moment. The mixture of lead and carbon (lead pyrophorus) resulting when tartrate of lead is heated in a test-tube until fumes cease to be evolved, spontaneously ignites when thrown into the air, and for the same reason. Many substances, solid and liquid, if sufficiently finely divided and liable to oxidation, and especially if exposed in a warm place, become hot and even occasionally burst into flame spontaneously. Oil on cotton waste, powdered charcoal, coal (especially if pyritic, porous, or powdered), resins in powder, and even flour and hay, are familiar illustrations of materials liable to "heat," char, or even burn spontaneously.

Note 2.—The student, having time and opportunity for the experiment, is advised to convert this sixteenth reaction into a roughly quantitative one, by way of realizing what has been stated (see again, the General Principles of Chemical Philosophy, pp. 29–60) respecting the action of chemical force on definite weights only of matter. Three tubes, similar to the oxide-tube shown in the engraving, should be prepared, the second being connected to the first, and the third to the second, by india-rubber tubing in the usual manner. The first tube should contain pieces of chloride of calcium to absorb any traces of moisture not retained by the sulphuric acid. The second tube (the ends of the small tube being temporarily closed by small corks) should be weighed in any ordinary scales which will turn with a quarter of or half a grain, and, the weight being noted, 160 grains of dry ferric oxide should be neatly placed in the middle of the tube. (The oxide, before being weighed, must be heated gently in a small crucible over a lamp to remove all traces of moisture.) The third tube should contain pieces of chloride of calcium to absorb the water produced in the reaction, and just before being connected should be weighed. The operation is now carried out. At its close, and when the middle tube is cold, the latter tube and the third tube are again weighed. The oxide-tube should weigh 48 grains less than before, and the terminal tube 54 grains more than before.

$$\underbrace{Fe_2O_3}_{(112+48)} + \underbrace{3H_2}_{6} = \underbrace{Fe_2}_{112} + \underbrace{3H_2O}_{54}$$

The operation is more quickly and easily performed if one-half or one-quarter of the weight of oxide be taken; in that case one-half or one-quarter of the weights of iron and of water will be obtained. Indeed any weight of oxide may be employed; the amount of iron and water resulting will be *always exactly proportionate* to the weights just mentioned. Thus 16 parts of oxide yield 11·2 of iron and 5·4 of water. Iron, hydrogen, and oxygen, always combine in proportions of 56, of 1, and of 16 respectively. Such facts justify us in agreeing that the symbol Fe shall stand for 56 parts by weight of iron, H for 1 part by weight of hydrogen, and O for 16 parts by weight of oxygen.

Dialysed Iron.

"*Liquor Ferri Dialysatus*, B.P.—This solution of Dialysed Iron, so called, is a solution of about 5 per cent. of highly basic ferric oxychloride or chloroxide of iron, from which most f the acidulous matter has been removed by dialysis." It is a clear dark reddish-brown liquid, free from any marked erruginous taste." Its specific gravity is about 1·047. *Vide* "Dialysis" in Index.)

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

(The iron occurring as a ferrous salt.)

First Analytical Reaction.—Pass sulphuretted hydrogen (H_2S) through a solution of a ferrous salt (*e.g.* ferrous sulphate) slightly acidulated by hydrochloric acid; no precipitate occurs. This is a valuable negative fact, as will be evident presently.

Second Analytical Reaction.—Add sulphydrate of ammonium (NH_4HS) to solution of a ferrous salt; a black precipitate (ferrous sulphide, FeS) falls.

$$FeSO_4 + 2NH_4HS = FeS + (NH_4)_2SO_4 + H_2S.$$

Third Analytical Reaction.—Add solution of ferrocyanide of potassium (yellow prussiate of potash), $K_4Fe''Cy_6$, or K_4Fcy'''' to solution of a ferrous salt; a precipitate ($K_2Fe''Fe'''Cy_6$, or $K_2Fe''Fcy$) falls, at first white or bluish grey, but rapidly becoming blue owing to absorption of oxygen.

Fourth Analytical Reaction.—To a ferrous salt add ferricyanide of potassium (red prussiate of potash, $K_6Fe'''_2Cy_{12}$, or K_6Fdcy); a precipitate falls ($Fe''_3Fe'''_2Cy_{12}$, or Fe''_3Fdcy) (Turnbull's blue) resembling prussian blue in colour.

Other Analytical Reactions.—The precipitates produced from ferrous solutions on the addition of alkaline carbonates, phosphates, and arseniates, as already described in the synthetical reactions of ferrous salts, are characteristic, and hence have a certain amount of analytical interest, but are inferior in this respect to the four reactions above mentioned.

Note.—Alkalies (potash, soda, or ammonia) are incomplete precipitants of ferrous salts, hence are almost useless as tests. To solution of a ferrous salt add ammonia (NH_4HO); on filtering off the whitish ferrous hydrate, and testing the solution with sulphydrate of ammonium, iron will still be found. To another portion of the ferrous solution add a few drops of nitric acid or excess of chlorine water, and boil; this converts the ferrous into ferric salt, and now alkalies will wholly remove the iron, as already twice seen during the performance of the synthetical experiments.

In actual analysis, the separation of iron as ferric hydrate is an operation of frequent performance. This is always accomplished by the addition of alkali, after (if the iron occurs as a ferrous salt) previous ebullition with a little nitric acid. Ferrocyanide and ferricyanide of potassium are the reagents used in distinguishing ferrous from ferric salts.

(The iron occurring as a ferric salt.)

Sixth Analytical Reaction.—Through a ferric solution (ferric chloride, *e.g.*) pass sulphuretted hydrogen; a white precipitate of the sulphur of the sulphuretted hydrogen falls. The ferric is simultaneously reduced to a ferrous salt, the latter remaining in solution. This reaction is of frequent occurrence in practical analysis:—$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2$.

Seventh Analytical Reaction.—Add sulphydrate of ammonium to a ferric solution; the latter is reduced to the ferrous state, and a black substance (ferrous sulphide, FeS) is precipitated as in the second analytical reaction, sulphur being set free.

Eighth Analytical Reaction.—To a ferric solution add ferrocyanide of potassium (K_4FeCy_6, or K_4Fcy''''); a precipitate of prussian blue (the common pigment) occurs ($Fe'''_43Fe''Cy_6$, or Fe'''_4Fcy_3'''').

Ninth Analytical Reaction.—To a ferric solution add solution of ferricyanide of potassium; no precipitate occurs, but the liquid is darkened to a brownish red, or to a greenish or olive hue, if the salts are not quite pure.

Tenth Analytical Reaction.—The production of a red precipitate (ferric hydrate) on adding alkalies to ferric salts. It is identical with the eleventh synthetical reaction.

Note.—This reaction illustrates the conventional character of the terms synthesis and analysis. It is of equal importance to the manufacturer and the analyst, and is synthetical or analytical according to the intention with which it is performed.

Other ferric reactions have occasional analytical interest.

In neutral ferric solutions the tannic acid in aqueous infusion of galls occasions a bluish-black inky precipitate, the basis of most black writing-inks.——(The *Mistura Ferri Aromatica* of the British Pharmacopœia, made by digesting metallic iron in an infusion of various vegetable substances, contains tannate, or rather tannates of iron; it is commonly known in Ireland by the name of Heberden's Ink, after the physician by whom it was first used. It contains about 1 grain of iron in 1 pint.)——*Sulphocyanate of Potassium* (KCyS) causes the formation of ferric sulphocyanate, which is of a deep blood-red colour. There is no normal ferric carbonate; alkaline carbonates cause the precipitation of ferric hydrate, whilst carbonic acid gas escapes.

Note.—Cyanogen (CN, or Cy'), ferro-cyanogen (FeC_6N_6, or $FeCy_6$, or simply Fcy''''), and ferri-cyanogen (Fe_2Cy_{12}, or $Fdcy^{vi}$) are radicals which play the part of non-metallic elements, just as ammonium in its chemical relations resembles the metallic elements. They will be referred to again.

Memorandum.—The reader must on no account omit to write out equations or diagrams expressive of each of the reactions of iron, analytical as well as synthetical. It is assumed that this has already been done immediately after each reaction has been performed.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING **ONE** OF THE METALS, ZINC, ALUMINIUM, IRON.

Add solution of ammonia gradually:—

A dirty-green precipitate indicates iron in the state of a ferrous salt.

A red precipitate indicates iron in the state of a ferric salt.

A white precipitate, insoluble in excess, indicates the presence of an aluminium salt.

A white precipitate, soluble in excess, indicates zinc.

These results may be confirmed by the application of some of the other tests to fresh portions of the solution.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE METALS, ZINC, ALUMINIUM, IRON.

Boil about half a test-tubeful of the solution with a few drops of nitric acid. This insures the conversion of ferrous into ferric salts, and enables the next reagent (ammonia) *completely* to precipitate the iron. Add excess of ammonia, and shake the mixture. Filter.

<table>
<tr><td colspan="2">Precipitate
Al Fe.*
Dissolve in HCl, add excess of KHO, stir, filter.</td><td rowspan="2">Filtrate
Zn.
Test by NH_4HS (white ppt.).</td></tr>
<tr><td>Ppt.
Fe
(red ppt.).</td><td>Filtrate
Al.
Make slightly acid by HCl, and add excess of NH_4HO† (white ppt.).</td></tr>
</table>

* The aluminium precipitate (Al_26HO) is white, the iron (Fe_26HO) red. If the precipitate is red, iron must be and aluminium may be present; if white, iron is absent, and further operations on the ppt. are unnecessary.

This precipitate (Al_26HO and Fe_26HO) may also, if sufficient is at disposal, be analysed by simply well shaking a washed portion in a tube with solution of potash or soda; the hydrate of iron is not thereby affected, while the hydrate of aluminium is dissolved, and may be detected in the clear decanted fluid by neutralizing all alkali by a little excess of acid, and then adding excess of ammonia.

† Alumina, when in small quantity, is sometimes prevented from being precipitated by ammonia through the presence of organic matter derived from the filter paper by action of the potash. In cases of doubt, therefore, before adding ammonia boil the liquid with a little nitric acid, which destroys any organic matter. Avoid *great* excess of ammonia.

Note 1.—If iron is present, portions of the original solution must be tested by ferricyanide of potassium for ferrous, and by ferrocyanide for ferric salts; dark-blue precipitates with both indicate both ferrous and ferric salts.

Note 2.—If no ferrous salt is present, ebullition with nitric acid is unnecessary. It is perhaps therefore advisable always to determine this point *previously* by testing a little of the original solution with ferricyanide; if no blue precipitate occurs, the nitric-acid treatment may be omitted.

CHART FOR ALL METALS HITHERTO CONSIDERED.

The following Table (*vide* p. 185) is perhaps the best, but not the only adaptation of the ordinary reactions to systematic analysis. In it the analytical scheme for the third group is added to that of the first two groups. As before, analysis is commenced by the addition of chloride of ammonium to prevent partial precipitation of magnesium, and by ammonia to neutralize any acid—for acid destroys the group-precipitant, sulphydrate of ammonium, preventing its useful action and causing a precipitation of any free sulphur it may contain. Any precipitate by the ammonia may be disregarded, for the sulphydrate attacks both solid and liquid.

Note.—When a test gives no reaction, absence of the body sought may fairly be inferred. If a group-test (that is, a test which precipitates a group of substances) gives no reaction, the analyst is saved the trouble of looking for any of the members of that group.

QUESTIONS AND EXERCISES.

Name the chief ores of iron.—How is the metal obtained from the ores?—What is the chemical difference between cast iron, wrought iron, and steel?—Explain the process of "welding."—What is the nature of chalybeate waters?—Illustrate by formulæ the difference between ferrous and ferric salts.—Under what different circumstances may the atom of iron be considered to exert bivalent, trivalent, and sexivalent activity? Write a paragraph on the nomenclature of iron salts.—Give a diagram of the process for the preparation of ferrous sulphate.—In what respects do the official Sulphate of Iron, Granulated Sulphate of Iron, and dried Sulphate of Iron differ?—How is ferrous sulphate obtained on the large scale?—Give the chemical names of white, green, and blue vitriol.—Why does ferrous sulphate become brown on exposure to air?—Show the formation of Ferrous Carbonate by a diagram.—Describe the

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Add NH_4Cl; NH_4HO; NH_4HS; warm, filter.

<table>
<tr>
<td colspan="3">Precipitate
Fe Al Zn.
Wash, dissolve in HCl,* boil (to remove H_2S), filter (to remove S), add excess of KHO,† stir, filter.</td>
<td colspan="4">Filtrate
Ba Ca Mg NH_4 Na K.
Add $(NH_4)_2CO_3$, boil, filter.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Fe
(test orig. sol. by K_4Fcy and K_6Fdcy).</td>
<td colspan="2">Filtrate
Al Zn.
Neutralize with HCl, add NH_4HO, stir, filter.</td>
<td colspan="2">Ppt.
Ba Ca.
Dissolve in $HC_2H_3O_2$, add K_2CrO_4, filter.</td>
<td colspan="2">Filtrate
Mg NH_4 Na K.
Add $(NH_4)_2HPO_4$, stir, filter.</td>
</tr>
<tr>
<td>Ppt.
Al
(white).</td>
<td>Filtrate
Zn
Add NH_4HS
(white ppt.).</td>
<td>Ppt.
Ba
(yellow).</td>
<td>Filtrate
Ca
Add
$(NH_4)_2C_2O_4$
(white ppt.).</td>
<td>Ppt.
Mg
(white).</td>
<td>Filtrate
NH_4 Na K.
Evap., ignite, dissolve.
Na by flame; K by $PtCl_4$: orig. sol. for NH_4.</td>
</tr>
</table>

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* Add, also, a few drops of HNO_3 if iron be present—*i.e.*, if the ppt. be black. (*Vide* notes on pp. 180 and 183.)

† Or add excess of ammonia, filter, and test filtrate for zinc. The hydrates of iron and aluminium may then be separated by an alkali, as described in the footnote to the previous Table (p. 183).

action of atmospheric oxygen on ferrous carbonate; can the effect be prevented?—In what order would you mix the ingredients of *Mistura Ferri Composita*, and why?—Write out an equation illustrative of the formation of the official Phosphate of Iron.—Why is bicarbonate of sodium used in the preparation of ferrous phosphate?—Name four compounds of iron which may be formed by the direct union of their elements.—Give the official method for the preparation of Solution of Ferric Chloride.—Of what use is the spirit in Tincture of Perchloride of Iron?—How may Ferrous be converted into Ferric Sulphate?—What is the formula of Ferric Acetate? and how is it prepared for use in pharmacy?—Give the formula for *Ferri Peroxidum Hydratum*, B.P.—How does Ferric Hydrate act as an antidote to arsenic?—What are the properties of anhydrous ferric oxide?—What are the general characters and mode of production of the medicinal scale preparations of iron?—In what state is the iron in *Vinum Ferri*, B.P.?—What other form of Wine of Iron is official?—Give a diagram showing the formation of Ferric Nitrate.—Work out a sum showing how much ferric oxide will yield, theoretically, one hundredweight of iron. *Ans.*, 160 lbs.—Explain the action of the following reagents for iron, distinguishing between ferrous and ferric reactions, and illustrating each by an equation or a diagram:—*a*. Sulphydrate of ammonium. *b*. Ferrocyanide of potassium. *c*. Ferricyanide of potassium. *d*. Caustic alkalies. *e*. Sulphocyanate of potassium.—Describe the action of ammonia on salts of iron, aluminium, and zinc respectively.—What precautions must be used in testing for calcium a solution containing iron?—How is magnesium detected in the presence of zinc?—How is aluminium detected in presence of magnesium?—Draw up a scheme for the analysis of an aqueous liquid containing salts of iron, barium, and potassium.—How may zinc, magnesium, and ammonium be consecutively removed from aqueous solution?

ARSENIUM, AND STIBIUM OR ANTIMONY.

These elements resemble metals in appearance and in the character of some of their compounds; but they are still more closely allied to the non-metals phosphorus and nitrogen. Their atoms are quinquivalent (As^{v}, Sb^{v}), as seen in arsenic anhydride (As_2O_5) and pentachloride of antimony ($SbCl_5$), but usually exert trivalent activity only (As''', Sb'''), as seen in the hydrogen and other compounds (AsH_3, $AsCl_3$, $AsBr_3$, AsI_3). The hydrogen compounds of the four members of this group have the formulæ NH_3, PH_3, AsH_3, SbH_3. A few preparations of these two elements are used in medicine; but all are more or less powerful poisons, and hence have considerable toxicological interest.

Arsenium is an exception to the rule that the atomic weights (taken in grains, grammes, or other weights) of elements, under similar circumstances of temperature and pressure, give equal volumes of vapour, the equivalent weight

(75) of arsenium only occupying half such a volume. Hence while the molecular weights (that is, double the atomic weights) of oxygen ($O_2=32$), hydrogen ($H_2=2$), nitrogen ($N_2=28$), etc., give a similar bulk of vapour at any given temperature and pressure, the double atomic weight of arsenium ($As_2=150$), at the same temperature and pressure, only affords half this bulk. It would appear, therefore, that the molecule of arsenium contains four atoms, and that its formula is As_4. As in the case of sulphur, however, arsenium, in the state ordinarily known to us, may be abnormal, and conditions yet be found in which the molecular weight is double (instead of quadruple) the atomic weight.

From observed analogy between the two metals, the molecular constitution of stibium is probably similar to that of arsenium.

ARSENIUM.

Symbol, As. Atomic weight, 75.

Sources.—Arsenical ores are frequently met with in Nature, the commonest being the arsenio-sulphide of iron (FeSAs). This "mispickel" is roasted in a current of air, the oxygen of which, combining with the arsenium, forms common *white arsenic*, arsenious oxide, sometimes called *anhydrous arsenious acid*, or, better, *arsenious anhydride* (As_2O_3, or, perhaps, As_4O_6), *Acidum Arseniosum*, B.P., which is condensed in chambers or long flues. It commonly "occurs as a heavy white powder, or in sublimed masses, which usually present a stratified appearance, caused by the existence of separate layers, differing from each other in degrees of opacity." The vitreous or amorphous arsenic is far more soluble than the crystalline variety, and in other respects they differ in properties. Such differences between the crystalline and amorphous varieties of an element or compound are not infrequent: they have not yet been satisfactorily explained. *Realgar* (red algar) is the red native sulphide (As_2S_2), and orpiment (*auripigmentum*, the golden pigment), the yellow native sulphide (As_2S_3) of arsenium. The iodide of arsenium (AsI_3), *Arsenii Iodidum*, B.P., may be made from its elements or by dissolving white arsenic in aqueous hydriodic acid and evaporating. It occurs in "small orange-coloured crystals, readily and almost entirely soluble in water and in rectified spirit. Its aqueous solution has a neutral reaction, and gives a yellow precipitate with sulphuretted hydrogen. Heated in a test-tube, it almost entirely volatilizes, violet vapours of iodine being set free." An aqueous solution of about 1 per cent. of this arsenious iodide and 1 per cent. of mercuric iodide forms the *Liquor Arsenii et Hydrargyri Iodidi*, B.P., or *Donovan's Solution.*

REACTIONS HAVING SYNTHETICAL INTEREST.

Alkaline Solution of Arsenic.

First Synthetical Reaction.—Boil a grain or two of powdered arsenic (As_2O_3) in water containing a little carbonate of potassium, and, if necessary, filter. The solution, coloured with compound tincture of lavender, and containing 1 per cent. of arsenic, forms the *Liquor Arsenicalis*, B.P. (*Fowler's Solution*).

Note.—This official solution does not generally contain arsenite of potassium; for the arsenic does not decompose the carbonate of potassium, or only after long boiling. From concentrated solutions carbonic acid gas is more quickly eliminated.

Arsenious Acid and other Arsenites.

Arsenic, or *arsenious anhydride* (the so-called arsenious acid), when dissolved in water is said to yield true arsenious acid (H_3AsO_3), the arsenite of hydrogen.

$$\underset{\text{Arsenious anhydride.}}{As_2O_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Arsenious acid.}}{2H_3AsO_3}$$

When arsenic is dissolved in excess of solutions of potash or soda, arsenites are formed having the formulæ KH_2AsO_3 and NaH_2AsO_3. Boiled with excess of arsenic, one molecule of those salts combines with one of the arsenic. The usual character of such compounds is that of oily alkaline liquids.

Arsenic fused with alkaline carbonates yields pyroarsenites ($Na_4As_2O_7$ or $K_4As_2O_7$) and metallic arsenium. Arsenites have the general formula R'_3AsO_3.

Acid Solution of Arsenic.

Second Synthetical Reaction.—Boil arsenic with diluted hydrochloric acid. Such a solution made with prescribed proportions of acid and water, and containing 1 per cent. of arsenic (As_2O_3), forms the *Liquor Arsenici Hydrochloricus*, B.P. (*De Valangin's Solution* contains a grain and a half per ounce.)

Note.—No decomposition occurs in this experiment. The liquid is simply a solution of arsenic in the acid. The two solutions may be preserved for analytical operations.

Mem.—The practical student should boil arsenic in water only, and thus have an acid, alkaline, and aqueous solution for analytical comparison.

Arsenium.

Third Synthetical Reaction.—Place a grain or less of arsenic at the bottom of a narrow test-tube, cover it with about half an inch or an inch of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a flame, the mouth being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red-hot; then heat the bottom of the tube. The arsenic will sublime, become deoxidized by the charcoal, carbonic oxide being formed, and the element *arsenium*, sometimes termed *arsenicum*, and also formerly called *arsenic*, be deposited in the cooler part of the tube as a dark mirror-like metallic incrustation.

There is a characteristic odour, resembling garlic, emitted during this operation, probably due to a partially oxidized trace of arsenium which escapes from the tube; for arsenic does not give this odour; moreover, arsenium being a freely oxidizable element, its vaporous particles could scarcely exist in the air in an entirely unoxidized state.

Metallic arsenium may be obtained in large quantities by the above process if the operation be conducted in vessels of commensurate size. But performed with great care, in narrow tubes, using not charcoal alone, but *black flux* (a mixture of charcoal and carbonate of potassium obtained by heating acid tartrate of potassium in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odour and the formation of the mirror-like ring being highly characteristic of arsenium. Compounds of mercury and antimony, however, give sublimates which may be mistaken for arsenium.

Arsen′ic Acid and other Arseniates.

Fourth Synthetical Reaction.—Boil a grain or two of arsenic with a few drops of nitric acid until red fumes cease to be evolved; evaporate the solution in a small dish to dryness, to remove excess of nitric acid; dissolve the residue in water: the product is Arsen′ic Acid (H_3AsO_4).

Arsenic acid, when strongly heated, loses the elements of water, and arsenic anhydride remains (As_2O_5).

Arsenic anhydride readily absorbs water and becomes arsenic acid (H_3AsO_4). Arsenic acid is reduced to arsenious by the action of sulphurous acid ($H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$).

Salts analagous to arsenic acid, the arseniate of hydrogen, are termed *arseniates*, and have the general formula R'_3AsO_4. The ammonium arseniate, $(NH_4)_2HAsO_4$, may be made by neutralizing arsenic acid with ammonia. Its solution in water forms a useful reagent. Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

Arsenite and arseniate of sodium are used in the cleansing-operations of the calico-printer.

Pyroarseniate and Arseniate of Sodium.

Fifth Synthetical Reaction.—Fuse two or three grains of common white arsenic (As_2O_3) with nitrate of sodium ($NaNO_3$) and dried carbonate of sodium (Na_2CO_3) in a porcelain crucible, and dissolve the mass in water; solution of arseniate of sodium (Na_2HAsO_4) results.

$$\underset{\text{Arsenic.}}{As_2O_3} + \underset{\text{Nitrate of sodium.}}{2NaNO_3} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Pyroarseniate of sodium.}}{Na_4As_2O_7} + \underset{\text{Nitrous anhydride.}}{N_2O_3} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

The official proportions are 10 of arsenic to 8½ of nitrate of sodium and 5½ of dried carbonate, each powdered, the whole well mixed, fused in a crucible at a red heat till effervescence ceases, and the liquid poured out on a slab. The product is pyroarseniate of sodium ($Na_4As_2O_7$). Dissolved in water, crystallized, and dried, the salt has the formula $Na_2HAsO_4, 7H_2O$ (*Sodii Arsenias*, B.P.), the old Arseniate of Soda.

$$Na_4As_2O_7 \quad + \quad 15H_2O \quad = \quad 2(Na_2HAsO_4, 7H_2O).$$

Heated to 300° F., the crystals lose all water. A solution of 1 per cent. of the anhydrous salt (Na_2HAsO_4) in water, forms the *Liquor Sodii Arseniatis*, B.P. It has about half the arsenical strength of *Liquor Arsenicalis*, B.P. The anhydrous salt is used because the crystallized is of somewhat uncertain composition. The fresh crystals are represented by the formula $Na_2HAsO_4, 12H_2O$ (=53·7 per cent. of water); these soon effloresce and yield a stable salt having the formula $Na_2HAsO_4, 7H_2O$ (=40·4 per cent. of water). To avoid the possible employment of a mixture of these bodies, the invariable anhydrous salt is officially used, constancy in the strength of a powerful preparation being thereby secured.

The student will find useful practice in verifying, by calculation, the above numbers representing the centesimal proportion of water in the two arseniates of sodium. This will be easy if what has already been stated respecting a symbol representing a number as well as a name, and the remarks concerning molecular weight, be remembered.

The shape of each of the two varieties of arseniate of sodium ($Na_2HAsO_4, 12H_2O$, and $Na_2HAsO_4,7H_2O$) is identical with that of the corresponding phosphate of sodium ($Na_2HPO_4, 12H_2O$, and $Na_2HPO_4, 7H_2O$); the structure of the molecule of the 12-arseniate is the same as that of the 12-phosphate, and the 7-arseniate as that of the 7-phosphate; the two former are isomorphous, the two latter are isomorphous. This is only one instance of the strong analogy of arsenium and its compounds with phosphorus and its corresponding compounds. The preparation and characters of the next substance, arseniate of iron, will remind the learner of phosphate of iron.

Arseniate of Iron. Ferrous Arseniate.

Sixth Synthetical Reaction.—To a hot solution of arseniate of sodium add a hot solution of ferrous sulphate and a little solution of bicarbonate of sodium; a precipitate of ferrous arseniate occurs (Fe_32AsO_4) (*Ferri Arsenias*, B.P.). On a larger scale, $15\frac{3}{4}$ parts of dried arseniate dissolved in 100 of hot water, and $20\frac{3}{4}$ of sulphate in 120 of hot water, with $4\frac{1}{2}$ of bicarbonate, may be employed. The precipitate should be collected on a calico filter, washed, squeezed, and dried at a low temperature (100° F.) over a water-bath, to avoid excessive oxidation.

$$\underset{\text{Arseniate of sodium.}}{2Na_2HAsO_4} + \underset{\text{Bicarbonate of sodium.}}{2NaHCO_3} + \underset{\text{Ferrous sulphate.}}{3FeSO_4} =$$

$$\underset{\text{Ferrous arseniate.}}{Fe_32AsO_4} + \underset{\text{Sulphate of sodium.}}{3Na_2SO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

The use of the bicarbonate of sodium is to ensure the absence of free sulphuric acid in the solution. This acid is a solvent of ferrous arseniate. It is impossible to prevent its separation if only the ferrous sulphate (three molecular weights) and arseniate of sodium (two molecular weights) be employed.

At the instant of precipitation ferrous arseniate is white, but rapidly becomes of a green or greenish-blue colour owing to absorption of oxygen and formation of a ferrosoferric arseniate. When dry, it is a tasteless, amorphous, much oxidized powder, soluble in acids.

The *Hydrides* and *Sulphides of Arsenium*, and the *Arsenites* and *Arseniates of Copper* and of *Silver*, are mentioned in the following analytical paragraphs.

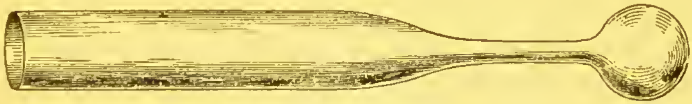
REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Repeat the third synthetical reaction, operating on not very much more arsenic than the bulk of a small pin's head, and using not charcoal alone, but the *black flux* already mentioned (p. 189) or a well-made and perfectly dry mixture of charcoal and carbonate of potassium, the latter best obtained by heating bicarbonate of potassium. The tube employed should be a narrow test-tube, or, better, a tube (easily made from glass tubing) having the form (Berzelius's) shown in fig. 33.

The arsenic and black flux are placed in the bulb of the tube, which is then heated in a flame; the arsenium condenses on the constricted portion of the tube. If now the bulb be carefully fused off in a flame, the arsenium may be chased up and down the narrower part of the tube until the air in the tube has re-oxidized it to arsenious anhydride.

If the operation has been performed in a less delicate manner in an ordinary test-tube, cut or break off portions of the tube containing the sublimate of arsenium, put them into a test-tube and heat the bottom of the latter, holding it nearly horizontally, and partially covering the mouth with the finger or thumb; the arsenium will absorb oxygen from the air in the tube, and the resulting arsenious anhydride (As_2O_3) be deposited on the cool part of the tube in brilliant, generally imperfect, octahedral crystals.

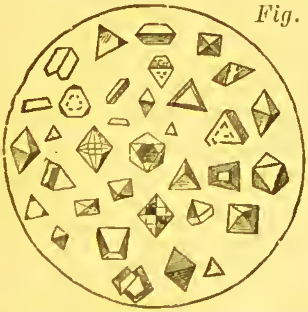
Fig. 33.



Microscopic Test.—Prove that the crystals are identical in form with those of common white arsenic by heating a grain or less of the latter in another test-tube, examining the two sublimates by a good lens or compound microscope.

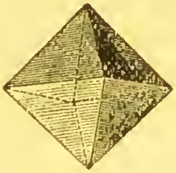
The appearance of a sublimate of arsenic is peculiar and

Fig. 34.



A SUBLIMATE OF ARSENIC (MAGNIFIED).

Fig. 34*a*.



A PERFECT OCTAHEDRON.

quite characteristic. The primary form of each crystal is an octahedron (ὀκτὼ, *okto*, eight; ἕδρα, *hedra*, side) (fig. 34*a*), or, rarely, a tetrahedron, and in a sublimate a few perfect octahedra are generally present. Usually, however, the crystals are modifications of octahedra such as are shown in fig. 34—which is drawn from actual sublimates.

Second Analytical Reaction.—Place a thin piece of copper, about a quarter-inch wide and half-inch long, in a solution of arsenic, acidified by hydrochloric acid, and boil (nitric acid must not be present, or the piece of metal will be dissolved); arsenium is deposited on the copper in a metallic condition. (*Memorandum.*—An equivalent proportion of copper goes into solution. The experiment forms an illustration of a class of chemical changes appropriately termed changes by *substitution.*) Pour off the supernatant liquid from the copper, wash the latter with water, dry the piece of metal by holding in the clean fingers and passing through a flame, and finally place it at the bottom of a clean, dry, narrow test-tube, or a Berzelius tube, and sublime as described in the last reaction, again noticing the form of the resulting crystals.

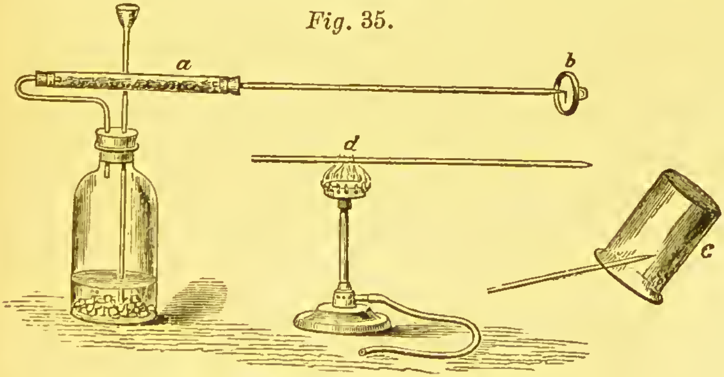
This is commonly known as Reinsch's test for arsenium, it having been introduced by Reinsch in 1843. The tube may be reserved for subsequent comparison with an antimonial sublimate.

Note.—Copper itself frequently contains arsenium, a fact that may not, perhaps, much trouble an operator so long as he is performing experiments in practical Chemistry merely for educational purposes; but when he engages in the analysis of bodies of unknown composition, he must assure himself that neither his apparatus nor materials already contain the element for which he is searching.

The detection of arsenium in metallic copper is best accomplished by distilling a mixture of a few grains of the sample with five or six times its weight of ferric hydrate or chloride (free from arsenium) and excess of hydrochloric acid. The arsenium is thus volatilized in the form of chloride of arsenium, and may be condensed in water and detected by sulphuretted hydrogen (6th Analytical Reaction) or Reinsch's test. The ferric chloride solution is, if necessary, freed from any trace of arsenium by evaporating once or twice to dryness with excess of hydrochloric acid.

Third Analytical Reaction.—The hydrogen test or "*Marsh's*" *test.*—Generate hydrogen in the usual way from water by zinc and sulphuric acid, a bottle of about four or six ounces capacity being used, and a funnel-tube and short delivery-tube passing through the cork in the usual manner (see following figure). Dry the escaping hydrogen (except in rough experiments, when it is unnecessary) by adapting to the delivery-tube, by a pierced cork, a short piece of wider tubing filled with fragments of chloride of calcium (*a*). To the opposite end of the drying-tube fit a piece of narrow tubing ten or twelve inches long, made of hard German glass, and having its aperture narrowed by drawing out in the flame of the blowpipe. When the hydrogen has been escaping for a sufficient number of minutes and at such a rate as to warrant the operator in concluding that *all the air originally existing in the bottle has been expelled*, set light to the jet, and then pour eight or ten drops of the aqueous solution of arsenic, or three or four drops of the acid or alkaline solution of arsenic, previously prepared, into the funnel-tube, washing the liquid into the generating-bottle with a little water. The arsenic is at once reduced to the state of arsenium, and the latter combines with some of the

Fig. 35.



THE HYDROGEN TEST FOR ARSENIUM.

hydrogen to form hydride of arsenium or arseniuretted hydrogen gas (AsH_3). Immediately hold a piece of earthenware or porcelain (the lid of a porcelain crucible (*b*) if at hand) in the hydrogen jet at the extremity of the delivery-tube; a brown spot of arsenium is deposited on the porcelain. Collect several of these spots, and retain them for future comparison with antimonial spots similarly obtained (p. 209).

The separation of arsenium in the flame is due to the decomposition of the arseniuretted hydrogen by the heat. The cool porcelain at once condenses the arsenium, and thus prevents its oxidation to white arsenic, which would otherwise take place at the outer edge of the flame.

Hold a small beaker (*c*), or wide test-tube, over the flame for a few minutes; a white film of arsenic (As_2O_3) will be slowly deposited, and may be further examined in contrast with a similar antimonial film (p. 209).

During these experiments the effect produced by the arsenical vapours on the colour of the hydrogen-flame will have been noticed; they give it a dull, livid, bluish tint. This is characteristic.

Apply the flame of a gas-lamp to the middle of the hard glass delivery-tube (*d*); the arseniuretted hydrogen, as before, is decomposed by the heat, but the liberated arsenium immediately condenses in the cool part of the tube, beyond the flame, as a dark metallic mirror. The tube may be removed and kept for comparison with an antimonial deposit (p. 209).

Note 1.—Zinc, like copper, frequently itself contains arsenium. When a specimen, free from arsenium, is met with, it should be reserved for analytical experiments, or a quantity of guaranteed purity should be purchased of the dealers in such articles. Sulphuric acid is more easily obtained free from arsenic.

Note 2.—In delicate and important applications of Marsh's test, magnesium may be substituted for zinc with safety, as arsenium has not yet been, and is not likely to be, found in magnesium. Magnesium in rods is convenient for this purpose, and may be obtained from most dealers in chemical substances. Both magnesium and zinc, if perfectly pure, react with acids extremely slowly; the addition of a very little perchloride of platinum, however, at once promotes an abundant evolution of hydrogen.

Note 3.—Sulphuric acid, which is often used for drying gases, decomposes arseniuretted hydrogen. Chloride of calcium is the appropriate desiccating agent for this gas.

Note 4.—The original apparatus proposed by Mr. Marsh, a pharmacist, of Woolwich, in 1836, was a U-shaped tube, one limb of which was short, and closed by a stopcock, so that the whole of a small quantity of arseniuretted hydrogen could be collected and be examined at leisure.

Fourth Analytical Reaction—Fleïtmann's test.—Generate hydrogen by heating in a test-tube, to near the boiling-point, a strong solution of caustic soda or potash and some pieces of zinc ($Zn + 2NaHO = H_2 + Na_2ZnO_2$—zincate of sodium). Add a drop of arsenical solution. Now spread over the mouth of the tube a cap of filter-paper moistened with one drop of solution of nitrate of silver. Again heat the tube, taking care that the liquid itself shall not spurt up on to the cap. A plug of cotton wool may even be placed in the mouth of the test-tube to prevent this spurting. The arsenic is reduced to arsenium, the latter uniting with the hydrogen, as in Marsh's test; and the arseniuretted hydrogen passing up through the cap reacts on the nitrate of silver, and gives rise to an excellent test by causing the production of a purplish-black spot (of silver).

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2.$$

Note 1.—This reaction is particularly valuable, enabling the analyst to quickly distinguish arsenium in the presence of its sister element antimony, which, although it combines with the hydrogen evolved from dilute acid and zinc, does not combine with the hydrogen evolved from solution of alkali and zinc, and therefore does not give the effect just described.

Note 2.—Aluminium answers as well as zinc for Fleitmann's test (Gatehouse), or magnesium may be used; or instead of zinc and alkali, weak sodium amalgam may be employed (Davy).

Fifth Analytical Reaction—Bettendorff's test.—To a solution of chloride of tin in strong hydrochloric acid add a very small quantity of any arsenical solution. Arsenium then separates, especially on the application of heat, giving the mixture a yellowish and then brownish hue or greyish-brown turbidity, or even a sediment of grey-brown flocks, according to the amount present. Much water prevents the reaction; its presence, therefore, must be avoided as far as possible; indeed, a liquid saturated by hydrochloric acid gas gives best results. Arsenic in sulphuric or hydrochloric acid or in tartar emetic, etc., may be detected by this method. Nitrates, such as subnitrate of bismuth, must first be heated with sulphuric acid to remove the nitric radical before applying this reduction-test for arsenium. The stannous is converted into stannic salt during the reaction.

Distinction between Arsenious and Arsen'ic combinations.—The above tests are those for arsenium, whether existing in the arsenious or arsenic condition; though the element is not so easily attacked when it is in the latter as when it is in the former state. Of the following reactions, that with nitrate of silver at once distinguishes arsenious acid and other arsenites from arsenic acid and other arseniates.

Mem.—The exact nature of all these analytical reactions will be more fully evident if the student will perseveringly trace them out by diagrams or equations.

Sixth Analytical Reaction.—Through an acidified solution of arsenic pass sulphuretted hydrogen; a yellow precipitate (sulphide of arsenium or arsenious sulphide, As_2S_3) quickly falls. Add an alkaline hydrate or sulphydrate to a portion of the precipitate; it readily dissolves. The precipitate consequently would not be obtained on passing sulphuretted hydrogen through an alkaline solution of arsenic. To another portion of the precipitate, well drained, add *strong* hydrochloric acid; it is insoluble—unlike sulphide of antimony. (Neither sulphide is soluble in the *weak* acid.)

Note 1.—Cadmium also affords a yellow sulphide in an acid solution by action of sulphuretted hydrogen; but this sulphide is insoluble in alkaline liquids. Under certain circumstances tin, too, yields a yellow sulphide, but tin is otherwise easily distinguished (*vide* "Tin" in Index).

Note 2.—A trace of sulphide of arsenium is sometimes met with in sulphur (distilled from arsenical pyrites). It may be detected by digesting the sulphur in solution of ammonia, filtering, and evaporating to dryness; a yellow residue of sulphide of arsenium is obtained if that substance be present.

Seventh Analytical Reaction.—Through an acidified solution of arsen'ic acid, or any other arseniate, pass a rapid current of sulphuretted hydrogen; a yellow precipitate (arsenic sulphide, As_2S_5) slowly falls. Brauner and Tornicek state that by a slow current the arsenic acid is gradually reduced to the arsenious, and a yellow precipitate of arsenious sulphide and sulphur ($As_2S_3 + S_2$) slowly falls. The precipitate is soluble in alkaline hydrates and sulphydrates. This reaction is more rapid if the solution be warmed.

Chemical Analogy of Sulphur and Oxygen. — The potassium arsenite and sulph-arsenite, arseniate and sulph-arseniate, have the composition represented by the following formulæ:—

$$\begin{array}{ll} K_3AsO_3 & K_3AsO_4 \\ K_3AsS_3 & K_3AsS_4\,; \end{array}$$

and the corresponding ammonium and sodium salts have a similar composition:—

$$6NH_4HS + As_2S_3 = 2(NH_4)_3AsS_3 + 3H_2S.$$
$$6NH_4HS + As_2S_5 = 2(NH_4)_3AsS_4 + 3H_2S.$$

Eighth Analytical Reaction.—To an aqueous solution of arsenic add two or three drops of solution of sulphate of copper, and then cautiously add diluted solution of ammonia, drop by drop, until a green precipitate is obtained. The production of this precipitate is characteristic of arsenium. To a portion of the mixture add an acid; the precipitate dissolves. To another portion add alkali; the precipitate dissolves. These two experiments show the advantage of testing a suspected arsenical solution by litmus-paper before applying this reaction—if acid, cautiously adding alkali; if alkaline, adding acid, till neutrality is obtained. Or a special copper reagent may be used: see a note to the Eleventh Analytical Reaction.

The precipitate is arsenite of copper ($Cu''HAsO_3$) or *Scheele's Green.* More or less pure, or mixed with acetate or, occasionally, carbonate of copper, it is used as a pigment under many names, such as Brunswick Green and Schweinfurth Green, by painters and others.

Ninth Analytical Reaction.—Apply the test just described to a solution of arsenic acid or other arseniate; a somewhat similar coloured precipitate (arseniate of copper) is obtained.

Tenth Analytical Reaction.—Repeat the eighth reaction, substituting nitrate of silver for sulphate of copper: in this case a *yellow* precipitate (arsenite of silver, Ag_3AsO_3) falls, also soluble in acids and alkalies.

Eleventh Analytical Reaction.—Apply the silver test to a solution of arsenic acid or other arseniate; a *chocolate-coloured* precipitate (arseniate of silver, Ag_3AsO_4) falls.

Copper and Silver Reagents for Arsenium.—The last four reactions may be performed with increased delicacy and certainty of result if the copper and silver reagents be previously prepared in the following manner:—To solution of pure sulphate of copper (about 1 part in 20 of water) add ammonia until the blue precipitate at first formed is nearly, but not quite, redissolved; filter and preserve the liquid as an arsenium reagent, labelling it *solution of ammonio-sulphate of copper* (B.P.). Treat solution of nitrate of silver (about 1 part in 40) in the same way, and label it *solution of ammonio-nitrate of silver* (B.P.). The composition of these two salts will be referred to subsequently.

Arsenious and Arsenic Compounds.—While many reagents may be used for the detection of arsenium, only nitrate of silver, as already stated, will readily indicate in which state the arsenium exists; for the two sulphides and the two copper precipitates, though differing in composition, resemble each other in appearance, whereas the two silver precipitates differ in colour as well as in composition.

Soluble arseniates give insoluble arseniates with solutions of salts of barium, calcium, zinc, and other metals.

In group-testing, arsenium, if existing as arsenic acid or other arseniate, is not readily affected by such tests as sulphuretted hydrogen or even by nascent hydrogen. Hence, if its presence in that state is suspected, the liquid under analysis should be warmed with a little sulphurous acid (*vide* p. 190) and then tested with sulphuretted hydrogen.

Antidote.—In cases of poisoning by arsenic or arsenical preparations, the most effective antidote is recently precipitated moist ferric hydrate administered as soon as possible. It is perhaps best administered in the form of a mixture of solution of perchloride of iron (*Liquor Ferri Perchloridi*, B.P.) with carbonate of sodium—two to three ounces of the former to about one ounce of the crystals of the latter. Instead of the carbonate of sodium, about a quarter of an ounce of calcined magnesia (*Magnesia*, B.P.) may be used. These quantities will render at least 10 grains of arsenic insoluble. Emetics should also be given, and the stomach-pump, or a common india-rubber tube worked as a siphon (page 120), be applied as quickly as possible.

The above statements regarding the antidote for arsenic may be verified by mixing the various substances together, filtering, and proving the absence of arsenium in the filtrate by applying some of the foregoing tests.

Mode of Action of the Antidote.—The action of the carbonate of sodium or the magnesia is to precipitate ferric hydrate (Fe_26HO)—chloride of sodium ($NaCl$) or of magnesium ($MgCl_2$) being formed, which are harmless, if not beneficial, under the circumstances. The reaction between the ferric hydrate and the arsenic results in the formation of insoluble ferrous arseniate. (See also p. 169.)

$$\underset{\text{Ferric hydrate.}}{2(Fe_26HO)} + \underset{\text{Arsenic.}}{As_2O_3} = \underset{\text{Ferrous arseniate.}}{Fe_32AsO_4} + \underset{\text{Water.}}{5H_2O} + \underset{\text{Ferrous hydrate.}}{Fe2HO}$$

The so-called Solution of Dialysed Iron (*see* Index) is also, as might be expected from its composition, an antidote to arsenic. It should be administered with a little bicarbonate of either sodium or potassium, or with magnesia, or with any other salt which serves to neutralize any acid that may be present.

QUESTIONS AND EXERCISES.

What is the formula of a molecule of arsenium?—In what form does arsenium occur in Nature?—Describe the characters of white arsenic. Name the official preparations of arsenium.—What compound of arsenium is contained in *Liquor Arsenicalis*, B.P., and *Liquor Arsenici Hydrochloricus*, B.P.?—By what method may arsenic be reduced to arsenium?—Give the formulæ of arsenious and arsenic acids and anhydrides.—Explain, by diagrams, the reactions which occur in converting arsenic into Arseniate of Sodium by the official process.—Why is anhydrous instead of crystallized arseniate of sodium employed in the preparation of *Liquor Sodii Arseniatis*, B.P.?—In the preparation of Arseniate of Iron from ferrous sulphate and arseniate of sodium, why is bicarbonate of sodium included? Describe the manipulations necessary to obtain arsenic in its characteristic crystalline form.—How is Reinsch's test for arsenium applied, and under what circumstances may its indications be fallacious?—Give the details of Marsh's test for arsenium, and the precautions to be observed. Explain the reactions by diagrams.—What peculiar value has Fleitmann's test for arsenium?—Describe the conditions under which sulphuretted hydrogen becomes a trustworthy test for arsenium.—How may a trace of sulphide of arsenium be detected in sulphur?—How are salts of copper and silver applied as reagents for the detection of arsenium?—How are arsenites distinguished from arseniates?—Mention the best antidote in case of poisoning by arsenic; explain the process by which it may be most quickly prepared, and describe its action.—Do you know of any other antidote to arsenic? If so, describe the mode of administration.

ANTIMONY.

Symbol, Sb (Stibium). Atomic weight, 120.

Source and Uses.—Antimony occurs in Nature chiefly as sulphide, Sb_2S_3. The *crude* or *black antimony* of pharmacy is this native sulphide freed from impurities by fusion: it has a striated, crystalline, lustrous fracture; subsequently powdered, and if it contains any soluble salt of arsenium, the latter removed by digestion in solution of ammonia, it forms the greyish-black crystalline *Antimonium Nigrum Purificatum*, B.P. The metal is obtained from the sulphide by roasting, the resulting oxide being reduced with charcoal and carbonate of sodium. The resulting scoria is known as *crocus* *of antimony* or *glass of antimony.* Metallic antimony is an important constituent of *Type-Metal*, *Britannia metal* (tea and coffee-pots, spoons, etc.), and the best varieties of *Pewter.* The old *pocula emetica*, or everlasting emetic cups, were made of antimony; wine kept in them for a day or two was said to have acquired emetic quality. The metal is not used in making official antimonial preparations, the sulphide alone being, directly or indirectly, employed for this purpose.

Antimony has very close chemical analogies with arsenium. Its atom, in the common salts, exerts trivalent activity (*e.g.* $SbCl_3$), but sometimes it is quinquivalent (*e.g.* $SbCl_5$).

Antimony, like arsenium, unites with iodine to form a tri-iodide (SbI_3). A bromide ($SbBr_3$) also is known.

REACTIONS HAVING SYNTHETICAL INTEREST.

Chloride of Antimony. Antimonious Chloride.

First Synthetical Reaction.—Boil half an ounce or less of sulphide of antimony with four or five times its weight of hydrochloric acid in a dish placed in a fume-chamber or in the open air; sulphuretted hydrogen is evolved and solution of chloride of antimony, $SbCl_3$, is obtained.

$$\underset{\substack{\text{Sulphide of}\\ \text{antimony.}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl} = \underset{\substack{\text{Chloride of}\\ \text{antimony.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{3H_2S}$$

This solution, cleared by subsidence, is what is commonly known as *Butter of Antimony* (*Liquor Antimonii Chloridi*, B.P.). If pure sulphide has been used in its preparation, the liquid is nearly colourless; but much of that met with in veterinary pharmacy is simply a by-product in the generation of sulphuretted hydrogen from native ferruginous sulphide of antimony and hydrochloric acid, and is more or less brown from the presence of chloride of iron. It not infrequently darkens in colour on keeping; this is due to absorption of oxygen from the air, and conversion of light-coloured ferrous into dark-brown ferric chloride or oxychloride.

True butter of antimony ($SbCl_3$) is obtained on evaporating the above solution to a low bulk, and distilling the residue. The butter condenses as a white crystalline semi-transparent mass in the neck of the retort; at the close of the operation it may be easily melted and run down into a bottle, which should be subsequently well stoppered.

Pentachloride of antimony ($SbCl_5$), or *antimonic chloride*, is a fuming liquid, obtained on passing chlorine over the lower chloride.

Oxychloride of Antimony. Antimonious Oxychloride.

Second Synthetical Reaction.—Boil the solution of chloride of antimony produced in the last reaction, and pour it into several ounces of water; a white precipitate of oxychloride of antimony ($2SbCl_3, 5Sb_2O_3$) falls, some chloride of antimony remaining in the supernatant acid liquid.

This precipitate is the old *pulvis Algarothi*, *pulvis angelicus*, or *mercurius vitæ*. It varies somewhat in composition, according to the amount of water with which the chloride may be mixed; but, on standing under water, gradually becomes crystalline, and has the composition above given.

$$\underset{\text{Chloride of antimony.}}{12SbCl_3} + \underset{\text{Water.}}{15H_2O} = \underset{\text{Oxychloride of antimony.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Hydrochloric acid.}}{30HCl}$$

Oxide of Antimony. Antimonious Oxide.

Well wash the precipitate with water by decantation (*vide* p. 117), and add solution of carbonate of sodium; the chloride remaining with the oxide is thus decomposed, and oxide of antimony (Sb_2O_3) alone remains. This is *Antimonii Oxidum*, B.P. It is of a light buff or greyish-white colour, or quite white if absolutely free from iron, insoluble in water, soluble in hydrochloric acid, fusible at a low red heat. The moist oxide of antimony may be well washed and employed for the next reaction. Or it may be dried over a water-bath, for at temperatures above 212° F. oxygen is absorbed, and other oxides of antimony formed. The presence of the latter is detected on boiling the powder in solution of acid tartrate of potassium, in which oxide of antimony (Sb_2O_3; Sb_4O_6?) is soluble, but *antimonic anhydride* (Sb_2O_5) and the double oxide, or so-called *antimonious anhydride* (Sb_4O_8), insoluble.

$$\underset{\text{Oxychloride of antimony.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Carbonate of sodium.}}{3Na_2CO_3} = \underset{\text{Oxide of antimony.}}{6Sb_2O_3} + \underset{\text{Chloride of sodium.}}{6NaCl} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

The higher oxide of antimony (Sb_2O_5), termed antimonic oxide or anhydride, corresponding with arsenic anhydride, is obtained on decomposing the pentachloride by water, or on boiling metallic antimony with nitric acid. The variety obtained from the chloride differs in saturating power from that obtained from the metal, and is termed metantimonic acid (μετὰ, *meta*, beyond).

Tartar Emetic.

Third Synthetical Reaction.—Mix the moist oxide of antimony obtained in the previous reaction with about an equal quantity of cream of tartar (6 of the latter to 5 of the dry oxide) and sufficient water to form a paste; set aside for a day to facilitate complete combination; boil the product with water, and filter; the resulting liquid contains the oxytartrate of antimony and potassium ($KSbOC_4H_4O_6$), potassio-tartrate of antimony, or tartarated antimony, or tartar emetic (emetic, from ἐμέω, *emeō*, I vomit; tartar, from Τάρταρος, *tartaros*, see Index).

$$\underset{\substack{\text{Acid tartrate}\\\text{of potassium.}}}{2KHC_4H_4O_6} + \underset{\substack{\text{Oxide of}\\\text{antimony.}}}{Sb_2O_3} = \underset{\text{Tartar emetic.}}{2KSbOC_4H_4O_6} + \underset{\text{Water.}}{H_2O}$$

On evaporation, the salt is obtained in colourless transparent triangular-faced crystals containing one molecular proportion of water to every two of anhydrous salt; forming the *Antimonium Tartaratum*, B.P. $(KSbOC_4H_4O_6)_2, H_2O$.

The formula for tartar emetic is apparently inconsistent with the general formula for tartrates ($R'R'C_4H_4O_6$); this will be subsequently fully explained in connection with Tartaric Acid. The salt appears to be an oxytartrate, $K'Sb'''O''(C_4H_4O_6)''$.

Tartar emetic is soluble in water, and slightly so in proof spirit. Dissolved in sherry wine, it forms the official *Vinum Antimoniale*, B.P. It may be externally applied as an ointment, *Unguentum Antimonii Tartarati*, B.P.

"Sulphurated Antimony" and other Antimony Oxysulphides.

Fourth Synthetical Reaction.—Boil a few grains of sulphide of antimony and of sulphur with solution of soda in a test-tube, and filter (or in larger vessels, 10 ounces of sulphide, 10 of sulphur, and $4\frac{1}{2}$ pints of the official solution of soda for 2 hours, frequently stirring, and occasionally replacing water lost by evaporation). Into the filtrate, before cool, stir diluted sulphuric acid until the liquid is slightly acid to test-paper; an orange-red precipitate, sulphurated antimony, the *Antimonium Sulphuratum*, B.P., falls; filter, wash, and dry over a water-bath. It is a mixture of the higher pentasulphide of antimony (Sb_2S_5) with a little oxide (Sb_2O_3, or possibly Sb_2O_5). The oxides result from the double decomposition of sulphides of antimony and caustic soda.

This is one of the many varieties of *mineral kermes*, so called from their similarity in colour to the *insect kermes*. *Kermes* is the name, now obsolete, of the *Coccus Ilicis*, a sort of cochineal-insect, full of reddish juice, and used for dyeing from the earliest times. The term *mineral kermes* was apparently applied originally to the amorphous or precipitated orange sulphide of antimony (Sb_2S_3). It afterwards included any oxysulphide and pentasulphide. A brownish-red variety may be prepared without the addition of any free sulphur; the colour of the precipitate is then affected by the temperature as well as state of dilution of the alkaline liquid when the acid is added. When this alkaline liquid is boiled, especially if long exposed to air, oxygen is absorbed by some of the antimony, whose sulphur uniting with the trisulphide forms a portion of the lighter yellow pentasulphide.

Explanation of processes.—The sulphides and oxides of antimony, like those of arsenium, react with the sulphides, hydrates, and oxides of certain metals to form salts of greater or less degree of solubility. Thus antimonite of sodium (Na_3SbO_3) is formed and remains in solution, and sulphantimonite of sodium (Na_3SbS_3) is formed and is deposited in brilliant yellow tetrahedral crystals when a hot alkaline solution of the sulphide of antimony is set aside to cool. Sulphur being present, the slightly soluble antimoniate of sodium (Na_3SbO_4) and sulphantimoniate of sodium (Na_3SbS_4) are produced.

$$\underset{\substack{\text{Sulphide of}\\\text{antimony.}}}{2Sb_2S_3} + \underset{\text{Soda.}}{6NaHO} = \underset{\substack{\text{Sulph-antimonite}\\\text{of sodium.}}}{2Na_3SbS_3} + \underset{\substack{\text{Antimonious}\\\text{oxide.}}}{Sb_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Antimonious oxide.}}{Sb_2O_3} + 6NaHO = \underset{\text{Antimonite of sodium.}}{2Na_3SbO_3} + 3H_2O$$

$$\underset{\substack{\text{Sulphide of}\\\text{antimony.}}}{2Sb_2S_3} + 2S_2 + 6NaHO = \underset{\substack{\text{Sulph-antimo-}\\\text{niate of sodium.}}}{2Na_3SbS_4} + \underset{\substack{\text{Antimonic}\\\text{oxide.}}}{Sb_2O_5} + H_2O + 2H_2S$$

$$\underset{\text{Antimonic oxide.}}{Sb_2O_5} + 6NaHO = \underset{\text{Antimoniate of sodium.}}{2Na_3SbO_4} + 3H_2O$$

In the hot solutions of these sulphur salts and oxygen salts, sulphides and oxides of antimony are soluble, and are reprecipitated in an indefinite state of combination, partially on cooling, or wholly on the addition of acid. The acid also decomposes the oxysalts with precipitation of oxides, and the sulphur salts with precipitation of sulphides of antimony. The acid should be added to the liquids before much oxysulphide has deposited (that is, before the solution is cool), if uniformity of product is desired.

$$\underset{\substack{\text{Sulph-antimonite}\\\text{of sodium.}}}{2Na_3SbS_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Sulphate}\\\text{of sodium.}}}{3Na_2SO_4} + \underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S}$$

$$\underset{\substack{\text{Antimonite}\\\text{of sodium.}}}{2Na_3SbO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Sulphate}\\\text{of sodium.}}}{3Na_2SO_4} + \underset{\substack{\text{Antimonious}\\\text{oxide.}}}{Sb_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\substack{\text{Sulph-antimoniate}\\\text{of sodium.}}}{2Na_3SbS_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Sulphate}\\\text{of sodium.}}}{3Na_2SO_4} + \underset{\substack{\text{Antimonic}\\\text{sulphide.}}}{Sb_2S_5} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S}$$

$$\underset{\substack{\text{Antimoniate}\\\text{of sodium.}}}{2Na_3SbO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Sulphate}\\\text{of sodium.}}}{3Na_2SO_4} + \underset{\substack{\text{Antimonic}\\\text{oxide.}}}{Sb_2O_5} + \underset{\text{Water.}}{3H_2O}$$

The oxides and sulphides indicated in these equations, together with excess of sulphide of antimony originally dissolved by the alkaline liquid, are all precipitated when the acid is added, and form the varieties of *kermes*. *Kermes* may be formed by fusion as well as by aqueous solution of the components. The student is strongly recommended carefully to study the foregoing paragraphs; for although neither the official nor any other variety of *kermes* is itself of much importance in modern practical pharmacy, a thoughtful consideration of their chemistry will, by revealing chemical actions and analogies that are general, aid in sowing the germs of chemical principles in the mind.

The previous four synthetical reactions illustrate the official processes for the respective substances. In pharmacy, the solution of chloride of antimony is only used in the preparation of oxide; the oxide, besides its use in the preparation of tartar emetic, is mixed with twice its weight of phosphate of calcium (purified bone-earth) to form *Pulvis Antimonialis*, B.P., or "James's Powder."

Sulphides and *Hydrides of Antimony* are incidentally mentioned in the following analytical paragraphs.

Reactions having Analytical Interest (Tests).

First Analytical Reaction.—Through an acidified antimonial solution pass sulphuretted hydrogen; an orange precipitate (amorphous sulphide of antimony) falls. It has the same composition as the crystalline black sulphide (Sb_2S_3), into which, indeed, when dried, it is quickly converted by heat. Like sulphide of arsenium, it is soluble in alkaline solutions. Collect a portion on a filter and, when well drained, add *strong* hydrochloric acid; it dissolves—unlike sulphide of arsenium.

A higher sulphide of antimony (Sb_2S_5), corresponding to the higher sulphide of arsenium, exists. It is formed on passing sulphuretted hydrogen through an acidified solution of the higher chloride ($SbCl_5$), or, less pure, on boiling black sulphide of antimony and sulphur with an alkali, and decomposing the resulting filtered liquid by an acid.

Note.—The arsenious and antimonious compounds are those chiefly employed in medicine; arseniates of sodium and iron are, however, sometimes employed. The arseniates and, rarely, an antimoniate are useful in analysis, and the antimonic chloride in chemical research. The higher compounds of both elements are noticed here chiefly to draw attention to the close analogy existing between arsenium and stibium, an analogy carried out in the numerous other compounds of those elements.

Second Analytical Reaction.—Dilute two or three drops of the solution of chloride of antimony with water; a white precipitate (oxychloride) occurs, the formation of which has been explained under the similar synthetical reaction. The occurrence of a precipitate under the circumstances distinguishes antimony from arsenium, but is a reaction that cannot be fully relied upon in analysis, because requiring the presence of too much material and the observance of too many conditions. Add a sufficient quantity of hydrochloric acid to dissolve the precipitate, and boil a piece of copper in the solution, as directed in the corresponding test for arsenium (*vide* page 196); antimony is deposited on the copper. Wash, dry, and heat the copper in a test-tube as before; the antimony, like the arsenium, is volatilized off the copper, and condenses on the side of the tube as white oxide; but the sublimate, from its low degree of volatility, condenses close to the copper; moreover, it is destitute of crystalline character.

Shake out the copper and boil water in the tube for several minutes. Do the same with the arsenical sublimate similarly obtained. The deposit of arsenic slowly dissolves, and may be recognised in the solution by ammonio-nitrate of silver; the antimonial sublimate is insoluble.

Third Analytical Reaction.—Perform the experiments described under Marsh's test for arsenium (pp. 195–6), carefully observing all the details there mentioned, but using a few drops of solution of chloride of antimony or tartar emetic instead of the arsenical solution. Antimoniuretted hydrogen, or hydride of antimony (SbH_3), is formed and decomposed in the same way as arseniuretted hydrogen.

To one of the arsenium spots on the porcelain lid (p. 196) add a drop of solution of "chloride of lime" (bleaching-powder); it quickly dissolves. Do the same with an antimony spot; it is unaffected. Heat more quickly causes the volatilization of an arsenium than an antimony spot; sulphydrate of ammonium more readily dissolves the antimony than the arsenium.

Boil water for several minutes in the beaker or wide test-tube containing the arsenious sublimate (p. 196); it slowly dissolves, and may be recognised in the solution by the yellow precipitate given on the addition of solution of ammonio-nitrate of silver. The antimonial sublimate, similarly treated, does not dissolve.

Pass a slow current of sulphuretted hydrogen through the delivery-tube removed from the hydrogen-apparatus (p. 196), and when the air may be considered to have been expelled from the tube, gently heat that portion containing the deposit of arsenium; the latter will be converted into a *yellow* sublimate of sulphide of arsenium. Remove the tube from the sulphuretted-hydrogen apparatus, and repeat the experiment with a similar antimony deposit; it is converted into *orange* sulphide of antimony, which, moreover, owing to inferior volatility, condenses nearer to the flame than sulphide of arsenium.

Pass dry hydrochloric acid gas through the two delivery-tubes. This is accomplished by adapting first one tube and then the other by a cork to a test-tube containing a few lumps of common salt, on which a little sulphuric acid is poured during the momentary removal of the cork. The sulphide of antimony dissolves and disappears; the sulphide of arsenium is unaffected.

Thorough perception of the chemistry of arsenium and antimony will be obtained on constructing equations or diagrams descriptive of each of the foregoing reactions.

Antidote.—The introduction of poisonous doses of antimonials into the stomach is fortunately quickly followed by vomiting. If vomiting has not occurred, or apparently to an insufficient extent, any form of tannic acid may be administered (infusion of tea, nutgalls, cinchona, oak-bark, or other astringent solutions or tinctures), an insoluble tannate of antimony being formed, and absorption of the poison consequently somewhat retarded. The stomach-pump or stomach-siphon must be applied as quickly as possible.

Recently precipitated moist ferric hydrate is also, according to T. and H. Smith, a perfect absorbent of antimony from its solutions, the chemical action being probably, they say, similar to that which takes place between ferric hydrate and arsenious anhydride. It may be given in the form of a mixture of perchloride of iron with either carbonate of sodium or other soluble carbonate or bicarbonate, or with magnesia.

These statements may be verified by mixing together the various substances, filtering, and testing the filtrate for antimony in the usual manner.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE ELEMENTS ARSENIUM AND ANTIMONY.

Acidify the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen:—

A *yellow* precipitate indicates arsenium;

An *orange* precipitate indicates antimony.

The result may be confirmed by the application of other tests.

DIRECTIONS FOR APPLYING THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF BOTH ARSENIUM AND ANTIMONY.

Acidify a small portion of the liquid with hydrochloric acid, and pass through it sulphuretted hydrogen.

Note 1.—If the precipitate by sulphuretted hydrogen is unmistakably orange, antimony may be put down as present, and arsenium only further sought by the application of Fleitmann's test to the solution of the sulphides in aqua regia * freed from sulphur by boiling, or, better, to the original solution.

Note 2.—Sulphide of antimony is far less readily soluble than sulphide of arsenium in solution of carbonate of ammonium. But this fact possesses limited analytical value; for the colour of the sulphides is already sufficient to distinguish the one from the other when they are unmixed; and when mixed, much sulphide of antimony will prevent a little sulphide of arsenium from being dissolved by the alkaline carbonate, while much sulphide of arsenium will carry a little sulphide of antimony into the solution. When the proportions are, apparently, from the colour of the precipitate, less wide, solution of carbonate of ammonium will be found useful in roughly separating the one sulphide from the other. On filtering and neutralizing the alkaline solution by an acid, the yellow sulphide of arsenium is reprecipitated. The orange sulphide of antimony will remain on the filter.

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* *Aqua Regia* is a mixture of four parts hydrochloric and three parts nitric acid. It was so called from its property of dissolving gold, the "king" of metals. Diluted with rather more than four times its bulk of water, it forms the *Acidum Nitro-hydrochloricum Dilutum*, B.P.

Note 3.—Solution of bisulphite of potassium is said by Wöhler to be a good reagent for separating the sulphides of arsenium and antimony, the former being soluble, the latter insoluble in the liquid.

Note 4.—Another reagent for separating the sulphides of arsenium and antimony is *strong* hydrochloric acid. As little water as possible must be present. On boiling, the sulphide of antimony dissolves, while the sulphide of arsenium remains insoluble. The liquid, slightly diluted, filtered, more water added, and sulphuretted hydrogen again transmitted, gives orange sulphide of antimony. The process should previously be tried on the precipitated mixed sulphides. The presence of arsenium may be confirmed by the application of Fleitmann's test to the original solution.

Note 5.—If the precipitate by sulphuretted hydrogen is unmistakably yellow, arsenium may be put down as present, and any antimony be detected by the previous or one of the following two processes. These two processes are rather long, and require much care in their performance; but are useful, because a small quantity of antimony in much arsenium, or *vice versâ*, may be detected by their means.

First process.—Generate hydrogen and pass it through a small wash-bottle containing solution of acetate of lead, to free the gas from any trace of sulphuretted hydrogen it may possess, and then through a dilute solution of nitrate of silver contained in a test-tube. When the apparatus is in good working order, pour into the generating bottle the solution to be examined, adding it gradually to prevent violent action. After the gas has been passing for five or ten minutes, examine the contents of the nitrate-of-silver tube; arsenium, if present, will be found in the solution in the state of arsenious acid,—

$$AsH_3 + 3H_2O + 6AgNO_3 = H_3AsO_3 + 6HNO_3 + 3Ag_2;$$

while antimony, if present, will be found in the black precipitate that has fallen, according to the following equation:

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

The arsenious radical may be detected in the clear, filtered, supernatant liquid, which still contains much nitrate of silver, by cautiously neutralizing with a very dilute solution of ammonia, or by adding a few drops of solution of ammonio-nitrate of silver, yellow arsenite of silver being produced. The antimony may be detected by washing the black precipitate, boiling it in an open dish with solution of tartaric acid, acidulating with hydrochloric acid, filtering and passing sulphuretted hydrogen through the solution,—the orange sulphide being precipitated. (Hofmann.)

Second process.—Obtain the metallic deposit in the middle of the delivery-tube as already described under Marsh's test. Act on the deposit by sulphuretted hydrogen gas, and then by hydrochloric acid gas, as detailed in the third analytical reaction of antimony (p. 210). If both arsenium and antimony are present, the deposit, after the action of sulphuretted hydrogen, will be found to be of two colours, the yellow sulphide of arsenium being usually farther removed from the heated portion of the tube than the orange sulphide of antimony. Moreover, subsequent action of hydrochloric acid gas causes disappearance of the antimonial deposit, which is converted into chloride of antimony and carried off in the stream of gas.

The chief objection to this process is the liability of the operator mistaking sulphur, deposited from the sulphuretted hydrogen gas by heat, for sulphide of arsenium. But the presence or absence of arsenium is easily confirmed by applying Fleitmann's test to the original solution, while the process is most useful for the detection of a small quantity of a salt of antimony when mixed with much arsenical matter. On the whole, Hofmann's method is to be recommended.

The laboratory student may now proceed to the analysis of aqueous solutions of salts of any of the metallic elements hitherto considered. The method followed may be that for the separation of the previous three groups, sulphuretted hydrogen being first passed through the solution to throw out arsenium and antimony. The whole scheme of analysis is given in the accompanying Table. Three or four solutions should be examined before proceeding to the next and last group of metals.

Learners who have no opportunity of working at practical analysis will gain much knowledge by endeavouring, not to remember, but, to understand these methods of separating elements from each other in a solution containing several compounds.

QUESTIONS AND EXERCISES.

What is the composition and source of "*Black Antimony*"?—In what alloys is metallic antimony a characteristic ingredient?—What is the quantivalence of antimony as far as indicated by the formulæ of the official preparations?—By a diagram show how "Butter of Antimony" is prepared.—Write out equations or diagrams expressive of the reactions which occur in converting chloride of antimony into oxide.—What is the formula of Tartar Emetic?—Explain the preparation of Oxysulphide of Antimony (*Antimonium Sulphuratum*, B.P.) by aid of diagrams?—Give a comparative statement of the tests for arsenium and antimony.—How is antimony detected in the presence of arsenium?—How may arsenium and iron be distinguished analytically?—Describe a method by which antimony, magnesium, and iron may be separated from each other.—Draw out a chart for the analysis of an aqueous liquid containing salts of arsenium, zinc, calcium, and ammonium.

COPPER, MERCURY, LEAD, SILVER.

These metals, like arsenium and antimony, are precipitated from acidified solutions by sulphuretted hydrogen, in the form of sulphides; but the sulphides, unlike those of arsenium and antimony, are insoluble in alkalies. The atom of

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.

Acidify with HCl, and pass H_2S through the solution; filter.

<table>
<tr><td rowspan="4">Precipitate
As Sb.
Wash, separate by carbonate of ammonium, or by strong hydrochloric acid; or dissolve in a few drops of hydrochloric and nitric acids, and examine by Hofmann's method (p. 212).</td><td colspan="7">Filtrate
Fe Al Zn Ba Ca Mg K Na NH_4.
Add NH_4HO*; NH_4HS; stir, filter.</td></tr>
<tr><td colspan="3">Precipitate†
Fe Al Zn.
Wash, dissolve in HCl, boil with HNO_3 (p. 183), add KHO in excess,‡ stir, filter.</td><td colspan="4">Filtrate
Ba Ca Mg K Na NH_4.
Add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td rowspan="2">Precipitate
Fe
Examine orig. solution for ferrous or ferric state.</td><td colspan="2">Filtrate
Al Zn.
Neut. by HCl, add NH_4HO, stir, filter.</td><td colspan="2">Precipitate
Ba Ca.
Dissolve in $HC_2H_3O_2$, add K_2CrO_4, filter.</td><td colspan="2">Filtrate
Mg K Na NH_4
Add $(NH_4)_2HPO_4$, shake, filter.</td></tr>
<tr><td>Ppt.
Al.</td><td>Sol.
Zn.</td><td>Precipitate
Ba.</td><td>Filtrate
Ca.</td><td>Precipitate
Mg.</td><td>Filtrate
NH_4NaK
(p. 185).</td></tr>
</table>

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* It is not usually necessary here to add NH_4Cl to keep Mg in solution, the HCl with some of the NH_4HO commonly giving sufficient NH_4Cl for this purpose.

† Much time may sometimes be saved by carefully remembering the colour of the various hydrates and sulphides precipitated. Thus, if the NH_4HS precipitate is white, iron cannot be present, and NH_4HO, for Al and Zn, may be at once added to the hydrochloric solution of the precipitate. The *group-tests* in this Table are H_2S, NH_4HS, and $(NH_4)_2CO_3$.

‡ The pupil should vary the process sometimes, as described in the footnotes on pages 180 and 181. The treatment of other groups should occasionally be varied. By remembering the reactions on which analytical processes are based, a pupil may often devise modified processes, and thus frequently save time, avoid working in one groove only, and acquire broader chemical views.

copper is usually bivalent, Cu''; mercury bivalent in the mercuric salts, Hg''; and univalent in the mercurous salts, Hg'; lead sometimes quadrivalent, Pb'''', but generally exerting only bivalent activity, Pb''; and silver univalent, Ag'.

COPPER.

Symbol, Cu. Atomic weight, 63·3.

Source.—The commonest ore of this metal is *copper pyrites*, a double sulphide of copper and iron, raised in Cornwall; Australia and Russia supply *malachite*, a mixed carbonate and hydrate; much ore is also imported from Spain and from South America. It is smelted in enormous quantities at Swansea, South Wales, a locality peculiarly fitted for the operation on account of its proximity to the coal-fields, and its position as a seaport—these united advantages insuring cheap fuel and freightage to the different metallurgical establishments. By Hollway's economical method of smelting copper pyrites and other sulphides, after the sulphide is once melted, air is driven, not over, as usual, but through the mass; the combustion of the sulphur then becomes self-supporting, and is greatly accelerated.

Alchemy.—The alchemists termed this metal *Venus*, perhaps on account of the beauty of its lustre, and gave it her symbol ♀, a compound hieroglyphic also indicating a mixture of gold ☉ and a certain hypothetical substance called acrimony ✠, the corrosive nature of which was symbolized by the points of a Maltese cross. To this day the blue show-bottle in the shop-window of the pharmacist is occasionally ornamented by such a symbol, indicating, possibly, that the blue liquid in the vessel is a preparation of copper.

Coinage.—The material of our "copper" coinage is now a bronze mixture composed, in 100 parts by weight, of 95 copper, 4 tin, and 1 zinc, the same as in the copper coinage of France. The penny is coined at the rate of 48 pence in one pound avoirdupois of 7,000 grains, or 453·6 grammes; the halfpenny at 80 in the pound avoirdupois, and the farthing at 160. These British bronze coins or tokens are a legal tender in payments to the amount of 1*s.*

Metallic Copper (*Cuprum*, B.P.) in the form of fine wire, about No. 25 of the Birmingham wire gauge, or 0·02 of an inch in diameter, is used in preparing *Spiritus Ætheris*

Nitrosi, B.P. *Copper Foil*, B.P., is "pure metallic copper, thin and bright."

Quantivalence.—Copper forms two classes of salts; in one the atom is bivalent (Cu''), in the other it exerts univalent activity (Cu'). The former are of primary importance to the student, the latter being for the most part unstable and wanting in technical interest. Their compounds are distinguished as *cupric* and *cuprous*. Cuprous iodide (Cu_2I_2) will be subsequently referred to as a convenient form in which to remove iodine from solution, while the formation of cuprous oxide (Cu_2O), under given circumstances, will come under notice as an indicator of the presence of sugar in a liquid.

REACTIONS HAVING SYNTHETICAL INTEREST.

The processes for the following salts include the only synthetical reactions having any medical or pharmaceutical interest:—(1) cupric oxide, the black oxide of copper, prepared by heating fragments of copper to low redness on a piece of earthenware in an open fire; (2) cupric sulphate, the common sulphate of copper, prepared by boiling black oxide and about an equal weight of sulphuric acid in water, filtering and setting aside the solution, so that crystals may form on cooling; and (3) ammonio-sulphates of copper, for the preparation of which see pages 199 and 219.

$$\underset{\text{Copper.}}{Cu_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Cupric oxide.}}{2CuO}$$

$$\underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Cupric sulphate.}}{CuSO_4} + \underset{\text{Water.}}{H_2O}$$

Sulphate of Copper (*Cupri Sulphas*, B.P.) ($CuSO_4$, $5H_2O$), *blue vitriol*, *blue stone*, or *cupric sulphate* is the only copper salt much used in pharmacy. It is a by-product in silver-refining ($2Ag_2SO_4 + Cu_2 = 2CuSO_4 + 2Ag_2$). A little is formed in roasting copper pyrites. In the latter case, some sulphide of iron and sulphide of copper are oxidized to sulphates; but the low red heat finally employed decomposes the sulphate of iron, while the sulphate of copper is unaffected; it is purified by crystallization from a hot aqueous solution, though frequently much sulphate of iron remains in the crystals. Sulphate of copper results on dissolving in diluted sulphuric acid the black oxide (CuO) obtained in annealing copper plates (*see* the foregoing equation); it may also be prepared by boiling copper with three times its weight of sulphuric acid ($2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$), diluting, filtering, evaporating, and crystallizing. In this process a little black sulphide of copper is formed.

Anhydrous Sulphate of Copper, B.P. ($CuSO_4$), is a yellowish-white powder prepared by depriving the ordinary blue crystals of sulphate of copper of their water of crystallization by exposing to a temperature of about 400° F. It is used in testing alcohol and similar spirituous liquids for water, becoming blue if the latter be present.

Nitrate of Copper (*Cupri Nitras*, B.P.), or *cupric nitrate*. Digest copper in diluted nitric acid. When action has ceased, evaporate and crystallize. If the crystals form at a temperature of 73° to 80° F., they are prismatic and trihydrous, $Cu(NO_3)_2 3H_2O$; at lower temperatures, tabular and hexahydrous, $Cu\,(NO_3)_2, 6H_2O$.

$$\underset{\text{Copper.}}{3Cu_2} + \underset{\text{Nitric acid.}}{16HNO_3} + \underset{\text{Water.}}{10H_2O} = \underset{\text{Nitrate of copper.}}{6Cu(NO_3)_2,(H_2O)_3} + \underset{\text{Nitric oxide.}}{4NO.}$$

Verdigris (from *verdi-gris*, Sp., green-grey) is a Subacetate or Oxyacetate of Copper (B.P.) ($Cu_2O2C_2H_3O_2$), obtained by exposing alternate layers of copper and fermenting refuse grape-husks to the action of air. Digested with twice its weight of acetic acid and a little water, the mixture being evaporated to dryness and the residue dissolved in water, it forms the official Solution of Acetate of Copper ($Cu2C_2H_3O_2$).

The modes of forming *Cupric Sulphide Hydrate*, *Oxide*, *Ferrocyanide* and *Arsenite*, as well as *Metallic Copper*, are incidentally alluded to in the following analytical paragraphs.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a copper salt (sulphate, for example); a black precipitate (cupric sulphide, CuS) falls.

Second Analytical Reaction.—To an aqueous copper solution add sulphydrate of ammonium; by this reagent, also, cupric sulphide is precipitated, insoluble in excess.

Note.—Cupric sulphide is not altogether insoluble in sulphydrate of ammonium if free ammonia or much ammoniacal salt be present; it is quite insoluble in the fixed alkaline sulphydrates.

Third Analytical Reaction.—Immerse a piece of iron or steel such as the point of a penknife or a piece of wire, in a few drops of copper solution; the copper is deposited, of characteristic colour, an equivalent quantity of iron passing into solution. By this reaction copper may be recovered on the large scale from waste solutions, old hoop or other scrap iron being thrown into the liquors.

Note.—This reaction furnishes another illustration of direct chemical *substitution.* As a matter of *fact*, 56 parts of the iron displace 63·3 of copper. As a matter of *theory*, in the whole mass of sulphate of copper each of the (theoretical) ultimate particles or *atoms* of copper weighing 63·3, is displaced by, or substituted by, one of the (theoretical) ultimate particles or *atoms* of iron, weighing 56, in the mass of iron. *Why* should the fact be as stated? We do not *know*; but the best, nay, the only, suggested explanation is that by Dalton, the one just applied, namely, "the atomic theory," the theory that matter is not infinitely divisible but composed of finite particles, conveniently termed *atoms.* Just as the bricks in a house might be displaced, one by one, by similarly shaped pieces of stone, without the structure, quâ structure, or architecture, being altered, so the copper atoms in the chemical structure termed sulphate of copper may be displaced, one by one, by iron atoms, the essential *structure* (at first $CuSO_4$, afterwards $FeSO_4$) not being altered. (In this particular case some other buildings, or wings, namely, $2H_2O$, are added to the structure at the same time, but this need not complicate the leading idea just offered.)

Fourth Analytical Reaction.—Add ammonia to a cupric solution; cupric hydrate ($Cu2HO$) of a light-blue colour is precipitated. Add excess of ammonia; the precipitate is redissolved, forming a blue solution of ammonio-salt of copper, so deep in colour as to render ammonia an exceedingly delicate reagent for this metal.

An ammonio-sulphate of copper may be obtained in large crystals by adding strongest solution of ammonia to powdered sulphate of copper until the salt is dissolved, placing the liquid in a test-glass or cylinder, cautiously pouring in twice its volume of strong alcohol or methylated spirit, taking care that the liquids do not become mixed, tying over the vessel with bladder, and setting aside for some weeks in a cool place. (Wittstein.) The constitution of ammonio-sulphate and other ammonio-salts of copper and corresponding salts of silver, will be alluded to in connection with "white precipitate," the official "ammoniated mercury."

Fifth Analytical Reaction.—Add solution of potash or soda to a cupric solution; cupric hydrate (Cu2HO) is precipitated, insoluble in excess. Boil the mixture in the test-tube; the hydrate is decomposed, losing the elements of water, and becoming the black anhydrous oxide (CuO).

Sixth Analytical Reaction.—Add solution of ferrocyanide of potassium (K_4Fcy) to an aqueous cupric solution; a reddish-brown precipitate (cupric ferrocyanide, Cu_2Fcy) falls. This is an extremely delicate test for copper.

Note.—Of course this reaction, like most chemical reactions, offers a case of chemical *substitution* (four univalent atoms of potassium, K_4, by two bivalent atoms of copper, Cu_2); it only is not quite so direct as that of the third reaction.

Seventh Analytical Reaction.—To a cupric solution add solution of arsenic, and cautiously neutralize with alkali; green cupric arsenite ($CuHAsO_3$) falls.

Note.—This precipitate has been mentioned already under arsenium. An arsenium salt is thus a test for copper, as a copper salt is for arsenium,—a remark that may obviously be extended to most analytical reactions; for the *body acted upon characteristically by a reagent is as good a test for the reagent as the reagent is for it;* indeed, it becomes a reagent when the other body is the object of search.

Most copper salts colour flame green, the chloride blue.

Antidotes.—In cases of poisoning by compounds of copper, iron filings should be administered, the action of which has just been explained (*see* Third Analytical Reaction). Ferrocyanide of potassium may also be given (*see* Sixth Analytical

Reaction). Albumen forms with copper a compound insoluble in water, hence raw eggs should be swallowed; vomiting being induced or the stomach-pump, or stomach-siphon, applied as speedily as possible.

QUESTIONS AND EXERCISES.

What are the analytical relations of copper, mercury, lead and silver to each other and to arsenium and antimony?—Name the sources of copper.—What proportion of copper is contained in English and French "copper" coins?—Give diagrams showing how Sulphate of Copper is prepared on the small and large scales.—Work out a sum showing how much Crystallized Sulphate of Copper may be obtained from 100 parts of sulphide. *Ans.* 261¼.—How may Oxide of Copper be prepared?—Mention the formula of Verdigris. Name a good chemical test for copper.—What is the analytical position of copper?—Mention the chief tests for copper.—How may copper be separated from arsenium?—Why is finely divided iron an antidote in poisoning by copper?

MERCURY.

Symbol, Hg. Atomic weight, 200.

Molecular weight, 200 (*not* double the atomic weight).

Source.—Mercury occurs in Nature as sulphide (HgS), forming the ore *cinnabar* (an Indian name expressive of something red), and is obtained from Spain, California, Eastern Hungary, China, Japan, and Peru.

Preparation.—The metal is separated by roasting off the sulphur and then distilling, or, better, distilling with lime, which combines with and retains the sulphur.

Properties.—Mercury (*Hydrargyrum*, B.P.) is a silver-white, lustrous metal, liquid at common temperatures. It boils at 662° F., and at -40° F. solidifies to a malleable mass of octahedral crystals. When quite free from other metals, it does not tarnish, and its globules roll freely over a sheet of white paper without leaving any streak or losing their spherical form.

Formula.—The formula of the mercury molecule is Hg and not Hg_2, because (at all events at the high temperature at which alone the weight of its vapour can be determined) two volumes, which, if hydrogen would weigh two parts (H_2) or oxygen thirty-two parts (O_2), in the case of mercury vapour weigh only two hundred parts (Hg); that is, only once the atomic weight, not twice. That 200, and not 100, is the atomic weight of mercury, is shown by the fact that 200 is the minimum proportion, relative to 1 of hydrogen, in which mercury combines, and by its relations to heat. Still it is difficult to imagine an atom existing in the free state in Nature; and the suggestion has been made that (as is proved to be the case with sulphur) mercury, as we know it, is in an abnormal condition, and that if the weight of its vapour could be taken at a lower temperature or under some other conditions, its molecular weight might be found to be 400. Similar remarks may be made respecting zinc and cadmium, the molecular weights of which, so far as we know, are identical with their atomic weights. At a *very* high temperature the weight of the vapour of iodine indicates a uniatomic molecule (I), at less elevated temperature two atoms in the molecule (I_2), a fact strongly supporting the inference that the real molecular weight of mercury is 400.

Medicinal Compounds.—The compounds of mercury used in medicine are all obtained from the metal. The metal itself, rubbed with chalk or with confection of roses and powdered liquorice-root, or with lard and suet, until globules are not visible *to the unaided eye*, is often used in medicine. The preparations are:—the *Hydrargyrum cum Creta*, B.P., or "Grey Powder;" *Pilula Hydrargyri*, B.P., or "Blue Pill;" and *Unguentum Hydrargyri*, B.P., or "Blue Ointment." There are also a Compound Ointment, a Plaster of Mercury, a Plaster of Ammoniacum and Mercury, a Liniment, and a Suppository, all official. Their therapeutic effects are probably due, not to the large quantity of metallic mercury in them, but to the small quantities of black and red oxide which occur in them through the action of the oxygen of the air on the finely divided metal. The proportion of oxide or oxides varies according to the age of the specimen. All these medicinal preparations of metallic mercury are indefinite and unsatisfactory, and that through no fault of the pharmacist. They much need investigation by pharmacologists and therapeutists. Here, as in many similar cases, if Medicine would first ascertain her own requirements, and then make them known, her handmaid Pharmacy would be found to be quite capable of supplying them.

Mercurous and Mercuric Compounds.—Mercury combines with other elements and radicals in two proportions: those compounds in which the acidulous radicals are in the lesser amount are termed *mercurous*, the higher being *mercuric*. Thus calomel ($HgCl$)* is mercurous chloride, while corrosive sublimate ($HgCl_2$) is mercuric chloride. In every pair of mercury compounds the mercuric contains *twice* as much complementary radical, in proportion to the mercury, as the mercurous.

Note on Nomenclature.—The remarks made concerning the two classes of iron salts, ferrous and ferric (p. 159), apply in the main to the two series of mercury salts. The latter are systematically distinguished in most modern works by the terms *mercurous* and *mercuric*. But the alteration of names of well-known substances in Medicine and Pharmacy, especially if they are poisonous substances, is liable to be attended by serious consequences to patients; therefore in the British Pharmacopœia, which includes only a few in comparison with the whole number of mercury salts, older and more strongly contrasted names are employed, thus:—

Systematic names.	Official names.
Mercuric iodide . . .	Red iodide of mercury.
Mercuric nitrate . . .	Nitrate of mercury.
Mercuric sulphate. . .	Persulphate of mercury.
Mercurous chloride . .	Subchloride of mercury.
Mercuric chloride. . .	Perchloride of mercury.
Red mercuric oxide .	Red oxide of mercury.
Yellow mercuric oxide	Yellow oxide of mercury.

Specific Gravity.—Mercury is 13·6 times as heavy as water.

Amalgams.—The compound formed on fusing metals together is usually termed an *alloy* (*ad* and *ligo*, I bind); but if mercury is a constituent, an *amalgam* (*μάλαγμα*, *malagma*, from *μαλάσσω*, *malasso*, I soften, the presence of mercury lowering the melting-point of such a mixture). Most metals, even hydrogen, according to Loew, form amalgams. "Electric amalgam" consists of 1 part each of tin and zinc and 3 parts mercury.

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* The specific gravity of the vapour of calomel, and the fact that the salt is *not* decomposed at the temperature at which its specific gravity is taken, indicate that the formula of calomel is $HgCl$, and not Hg_2Cl_2.

Reactions having Synthetical Interest.

The Two Iodides.

First Synthetical Reaction.—Rub together a small quantity of mercury and iodine, controlling the rapidity of combination by adding previously, and afterwards occasionally, a few drops of spirit of wine, which by evaporation absorbs heat, and thus keeps down the temperature. The product is either mercuric iodide, mercurous iodide, or a mixture of the two, as well as mercury or iodine, if excess of either has been employed. If the two elements have been previously weighed in single atomic proportions, 200 of mercury to 127 of iodine (about 8 to 5, or 1 ounce of mercury to 278 grains of iodine), the mercurous or green (greyish-green) iodide results, HgI; if in the proportion of one atom of mercury to two atoms of iodine (200 to twice 127, or about 4 to 5), the mercuric or red iodide, HgI_2, results—an iodide that is official, but made in another way (*see* p. 226). The green iodide should be made and dried (without heat) with as little exposure to light as possible. Red iodide may be removed from it by well washing with alcohol.

Mercurous iodide is decomposed slowly by light, and quickly by heat, into mercuric iodide and mercury. Mercuric iodide occurring as an impurity in mercurous iodide may be detected by digesting in ether (in which mercurous iodide is insoluble), filtering, and evaporating to dryness; mercuric iodide remains. Mercuric iodide is stable, and may be sublimed in scarlet crystals without decomposition. (For the mechanical details of the method by which a specimen of the crystals may be obtained, and the precautions to be observed, *vide* "corrosive sublimate," p. 230.)

Relation of Mercuric Iodide to Light.—In condensing, mercuric iodide is at first yellow, afterwards acquiring its characteristic scarlet colour. This may be shown by smearing or rubbing a sheet of white paper with the red iodide, and then holding the sheet before a fire or over a flame for a few seconds. As soon as the paper becomes hot the red instantly changes to yellow, and the salt does not quickly regain its red colour, even when cold, if the paper is carefully handled. But if a mark be made across the sheet by anything at hand, or the salt be pressed or rubbed in any way, the portions touched immediately return to the scarlet condition. According to Warington, this change is consequent upon rhomboidal crystals being converted into octahedra with a square base, and will serve as an excellent illustration of the influence of physical structure in causing colour. The yellow modification so acts on the rays of white light shining on its particles as to absorb the violet and reflect the complementary hue, the yellow, which, entering the eye of the observer, strikes his retina, and thus conveys to the brain the impression of yellowness; and the red modification, though actually the same chemical substance, is sufficiently different in the structure of its crystals to absorb the green constituent of white light and reflect the complementary ray, the red.

Illustration of the Chemical Law of Multiple Proportions (p. 46).—Applying the atomic theory to the above iodides, it will at once be apparent why mercury and iodine should combine in the proportion of 200 of mercury with either 127 or 254 of iodine, and not with any intermediate quantity. For it is part of that theory that masses are composed of atoms, and that atoms are indivisible, and that the weight of the atom of mercury is to that of iodine as 200 is to 127. Mercury and iodine can only combine, therefore, in atomic proportions, atom to atom (which is the same as 200 to 127), or one atom to two atoms (which is the same as 200 to 254). To attempt to combine them in any intermediate proportion would be useless, a mere mixture of the two iodides would result. A higher proportion of mercury than 200 to 127 of iodine gives but a mixture of mercurous iodide and mercury; a higher proportion of iodine than 254 to 200 of mercury gives but a mixture of mercuric iodide and iodine. Or, for example, 200 grains of 'mercury mixed with, say, 200 of iodine would yield 139 grains of mercurous iodide and 261 of mercuric iodide; for the 200 grains of mercury uniting with 127 of the iodine gives, for the moment, 327 grains of mercurous iodide and 73 of iodine still free. The 73 grains of iodine will immediately unite with 188 of the mercurous iodide (for if 127 of I require 327 of HgI to form HgI_2, 73 will require 188), and form 261 grains of mercuric iodide, diminishing the 327 grains of mercurous iodide to 139.

Note on Atomic Weight.—But the student will ask, *does* 127 represent the atomic position of iodine; relative, of course, to 1 of hydrogen, 16 of oxygen, and so on? Yes: because all synthetical and analytical operations with iodine show that 127 parts by weight is the quantity in which iodine migrates from compound to compound, or either displaces or is displaced by chlorine or bromine; secondly, because equal gaseous volumes of such elements contain equal numbers of atoms, and such equal volumes weighing 1, 16, 127, etc., each of the atoms of the respective elements must weigh 1, 16, 127, etc.; and thirdly, because similar numerical relationships are met with when the specific heats of the elements are determined, or when their electrical, optical, isomorphic and other relationships are studied. (*Vide* Index under the words, "Atomic," "Constitution," "Molecular," "Structure," etc.)

Preparation of Red Iodide of Mercury by Precipitation.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of iodide of potassium, drop by drop; a precipitate of mercuric iodide forms, and at first redissolves, but is permanent when sufficient iodide has been added. Continue the addition of iodide of potassium; the precipitate is redissolved.

$HgCl_2$	+	$2KI$	=	HgI_2	+	$2KCl$
Mercuric chloride.		Iodide of potassium.		Mercuric chloride.		Chloride of potassium.

Notes.—When first precipitated, mercuric iodide is yellowish-red, but soon changes to scarlet.—Its solubility either in solution of the mercuric salt or in solution of iodide of potassium renders the detection of a small quantity of a mercuric salt by iodide of potassium, or a small quantity of an iodide by a mercuric solution, difficult, and hence lessens the value of the reaction as a test.—But the reaction has synthetical interest, the method of precipitation being that adopted in the British Pharmacopœia (*Hydrargyri Iodidum Rubrum*, B.P.). Mercuric iodide thus made has the same composition as that prepared by direct combination of its elements. Equivalent proportions of the two salts must be used in making the preparation ($HgCl_2 = 271$; $2KI = 332$). About 4 parts of corrosive sublimate are dissolved in 50 or 60 of water (warmth quickens solution) and 5 of iodide of potassium in 15 or 20 of water, the solutions mixed and the precipitate collected on a filter, drained, washed twice with distilled water, and dried on a plate over a water-bath. Mercuric nitrate, which is more soluble and therefore somewhat more convenient for use on the large scale, may be used instead of the mercuric chloride.—The mercury in mercuric or mercurous iodide is set free, and sublimes in globules, on heating either powder with dried carbonate of sodium in a test-tube; the iodine may be detected by digesting with solution of soda, filtering, and to the solution of iodide of sodium thus formed adding starch-paste and acidulating with nitrous acid, when blue iodide of starch results. —Mercuric iodide is insoluble in water, slightly soluble in alcohol, tolerably soluble in ether.—Precipitated red iodide of mercury mixed with white wax, lard, and oil forms the *Unguentum Hydrargyri Iodidi Rubri*, B.P.

The Two Nitrates.

Second Synthetical Reaction.—Place a globule of mercury, about half the size of a pea, in a test-tube; add twenty or thirty drops of nitric acid; boil slowly until red fumes no longer form; set aside. On cooling, if a globule of mercury still remains in the tube, crystals of mercurous nitrate separate. These may be dissolved in water slightly acidulated by nitric acid. The solution may be retained for subsequent analytical operations.

$$3Hg + 4HNO_3 = 3HgNO_3 + 2H_2O + NO.$$

Third Synthetical Reaction.—Place mercury in *excess* of strong nitric acid, and warm the mixture; mercuric nitrate is formed, and will be deposited in crystals as the solution cools. Or, to crystals of mercurous nitrate add nitric acid, and boil until red fumes cease to form. Retain the product for a subsequent experiment.

When mercury and nitric acid are boiled together, mercuric nitrate is formed if the mercury be in excess, while mercuric nitrate is produced if the acid preponderate.

The mercuric nitrates vary somewhat in composition, according to the proportion, strength, and temperature of the acid used in their formation. A mercuric nitrate may be obtained having the formula $Hg2NO_3$.

$3Hg$	+	$8HNO_3$	=	$3(Hg2NO_3)$	+	$2NO$	+	$4H_2O$
Mercury.		Nitric acid.		Mercuric nitrate.		Nitric oxide.		Water.

Mercuric oxynitrates.—From the normal mercuric nitrate several oxynitrates may be obtained. Thus on merely evaporating a solution of mercuric nitrate, and cooling, crystals having the formula $Hg_6O_36NO_3$ are deposited. The latter, by washing with cold water, yield a *yellow* pulverulent oxynitrate, $Hg_6O_44NO_3$: mixed with lard, this has sometimes been used as an ointment. Boiled in water, the yellow gives a *brick-red* oxynitrate, $Hg_6O_52NO_3$.

The Pharmacopœial preparations of mercuric nitrate are *Liquor Hydrargyri Nitratis Acidus*, *Unguentum Hydrargyri Nitratis*, and *Unguentum Hydrargyri Nitratis Dilutum*. The former is made by placing four ounces of mercury in five fluid ounces of nitric acid diluted with an ounce and a half of water, and when the metal has dissolved, boiling gently for fifteen minutes.

The Two Sulphates.

Fourth Synthetical Reaction.—Boil two or three grains of mercury with a few drops of strong sulphuric acid in a test-tube, or, better, small dish, in a fume-chamber; sulphurous acid gas (SO_2) is evolved, and *mercuric sulphate* or *persulphate of mercury* (*Hydrargyri Persulphas*, B.P.) ($HgSO_4$) results—a white, heavy, crystalline powder.

Hg	+	$2H_2SO_4$	=	$HgSO_4$	+	SO_2	+	$2H_2O$
Mercury.		Sulphuric acid.		Mercuric sulphate.		Sulphurous acid gas.		Water.

Between two and three ounces of mercuric sulphate may be prepared from a fluid drachm of mercury and a fluid ounce of sulphuric acid boiled togethor in a small dish. These equal the official proportions. The operation is completed and any excess of acid removed by evaporating the mixture of metal and liquid to dryness, either in the open air or in a fume-chamber, sulphuric acid vapours being excessively irritating to the mucous membrane of the nose and throat; dry crystalline mercuric sulphate remains. If residual particles of mercury are observed, the mass should be damped with sulphuric acid and again heated.

By-products.—In chemical manufactories, secondary products, such as the sulphurous gas of the above reaction, are termed *by-products*, and, if of value, are utilized. In the present case the gas is of no immediate use, and is therefore allowed to escape. When very pure sulphurous acid gas is required for experiments on the small scale, this would be the best method of making it, a delivery-tube being adapted by a cork to the mouth of a flask containing the acid and metal. The sulphate of mercury would then become the by-product.

Mercuric oxysulphate.—Water decomposes mercuric sulphate into a soluble acid salt and an insoluble yellow oxysulphate ($Hg_3O_2SO_4$). The latter is called *Turpeth mineral*, from its resemblance in colour to *vegetable turpeth*, the powdered root of *Ipomœa turpethum*, an Indian substitute for jalap. The yellow sulphate of mercury was formerly official, but is now seldom used.

Fifth Synthetical Reaction.—Rub a portion of the dry mercuric sulphate of the previous reaction with as much mercury as it already contains; the product, when the two have thoroughly blended, is mercurous sulphate (Hg_2SO_4): it may be retained for a subsequent experiment.

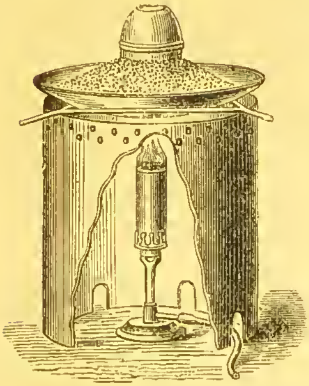
Molecular Weight.—The exact proportion of mercury to sulphate is merely a matter of calculation; for the combining proportion of a compound (if it possess any combining power), or its proportion for interchange or transposition (metathesis), is the sum of the combining proportions, or interchanging or transposing proportions, of its constituents. In other words, *the molecular weight of a compound is the sum of the atomic weights of its elements.* In accordance with this rule (deduced from the first law of chemical combination, p. 44), 296 of mercuric sulphate and 200 of mercury (about 3 to 2) are the proportions necessary to the formation of mercurous sulphate, $Hg\ (200) + HgSO_4\ (296) = Hg_2SO_4\ (496)$.

The Two Chlorides.

Sixth Synthetical Reaction.—Mix thoroughly a few grains of dry mercuric sulphate with about four-fifths its weight of chloride of sodium, and heat the mixture, slowly, in a test-tube in a fume-chamber; mercuric chloride ($HgCl_2$), or *corrosive sublimate*, bichloride or perchloride of mercury (*Hydrargyri Perchloridum*, B.P.), sublimes and condenses in the upper part of the tube in heavy colourless crystals or as a crystalline mass.

Somewhat larger quantities (in the proportion of 20 of sulphate to 16 of salt and, *vide infra*, 1 of black oxide of manganese) may be sublimed in a pair of two-ounce or three-ounce round-bottomed gallipots, the one inverted over the other, and the joint luted by moist fireclay (the powdered clay kneaded with water to the consistence of dough). The luting having been allowed to dry (somewhat slowly to avoid cracks), the pots are placed upright on a sand-tray (plate-shape answers very well), sand piled round the lower and a portion of the upper pot, and the whole heated over a good-sized gas-flame, for an hour or more in a fume-chamber (*see* fig. 36—pots raised to show joint). Red Iodide of Mercury, and Calomel, may be sublimed in the same way. The former requires less, the latter more, heat than corrosive sublimate.

Fig. 36.



SUBLIMATION.

$$\underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Chloride of sodium.}}{2NaCl} = \underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

Note.—If the mercuric sulphate contain any mercurous sulphate, some calomel may be formed. This result will be avoided if 2 or 3 per cent. of black oxide of manganese be previously mixed with the ingredients, the action of which is to eliminate chlorine from the excess of chloride of sodium used in the process, the chlorine converting any calomel into corrosive sublimate. Manganate of sodium and a lower oxide of manganese are simultaneously produced.

Precaution.—The operation is directed to be conducted with care in a fume-chamber, because the vapour of corrosive sublimate, which might possibly escape, is very acrid and highly poisonous. Mercuric chloride volatilizes, though extremely slowly and slightly, at warm temperatures.

Ten grains of perchloride of mercury and the same quantity of chloride of ammonium in one pint of water form the *Liquor Hydrargyri Perchloridi*, B.P. A dilute aqueous solution of perchloride of mercury is liable to decomposition, calomel being precipitated, water decomposed, hydrochloric acid formed, and oxygen gas evolved. The presence of excess of chloride of ammonium, with a portion of which the mercuric chloride forms a stable double salt, prevents the decomposition.

Seventh Synthetical Reaction.—Mix a few grains of the mercurous sulphate of the fifth reaction with about a third of its weight of chloride of sodium, and sublime in a test-tube; crystalline mercurous chloride ($HgCl$) or calomel (*Hydrargyri Subchloridum*, B.P.) results. Larger quantities may be prepared in the manner directed for corrosive sublimate, a somewhat higher temperature being employed: similar precautions must also be observed. The official proportions are 10 of mercuric sulphate to 7 of mercury and 5 of dry chloride of sodium. "Moisten the sulphate of mercury with some of the water, and rub it and the mercury together until globules are no longer visible; add the chloride of sodium, and thoroughly mix the whole by continued trituration. When dry, sublime by a suitable apparatus into a chamber of such size that the calomel, instead of adhering to its sides as a crystalline crust, shall fall as a fine (dull-white) powder on its floor. Wash this powder with boiling distilled water until the washings cease to be darkened by a drop of sulphydrate of ammonium. Finally, dry at a temperature not exceeding 212° F."

$$\underset{\text{Mercurous sulphate.}}{Hg_2SO_4} + \underset{\text{Chloride of sodium.}}{2NaCl} = \underset{\text{Mercurous chloride.}}{2HgCl} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4}$$

The term calomel (καλὸς, *kalos*, good, and μέλας, *melas*, black) probably was simply indicative of the esteem in which black sulphide of mercury was held, the compound to which the name calomel was first applied.

Test for corrosive sublimate in Calomel.—If the mercurous sulphate contain mercuric sulphate, some mercuric chloride will also be formed. Corrosive sublimate is soluble in water, calomel insoluble; the presence of the former may therefore be proved by boiling a few grains of the calomel in distilled water, filtering and testing by sulphuretted hydrogen or sulphydrate of ammonium as described hereafter. If corrosive sublimate be present, the whole bulk of the calomel must be washed with hot distilled water till the filtrate ceases to give any indications of mercury. Corrosive sublimate is more soluble in alcohol, and still more in ether, calomel insoluble. Ether in which calomel has been digested should therefore, after filtration, yield no residue on evaporation. Calomel is converted by hydrocyanic acid into mercuric salt, and a black powder readily yielding metallic mercury. Powell and Bayne have shown that a certain proportion of hydrochloric acid arrests this action.

Note.—The above process is that of the British Pharmacopœia; but calomel may also be made by other methods. Calomel mixed with lard forms the *Unguentum Hydrargyri Subchloridi*, B.P., and with sulphurated antimony, guaiacum resin, and castor-oil, the *Pilula Hydrargyri Subchloridi Composita*, B.P., or "Plummer's Pill."

The Two Oxides.

Eighth Synthetical Reaction.—Evaporate the mercuric nitrate of the third reaction to dryness in a small dish, in a fume-chamber or in the open air, if more than a few grains have been prepared, and heat the residue till no more fumes are evolved; red mercuric oxide (HgO), "Red Precipitate," the Red Oxide of Mercury (*Hydrargyri Oxidum Rubrum*, B.P.), remains.

$$\underset{\text{Mercuric nitrate.}}{2(\mathrm{Hg2NO_3})} = \underset{\text{Mercuric oxide.}}{2\mathrm{HgO}} + \underset{\text{Nitric peroxide.}}{4\mathrm{NO_2}} + \underset{\text{Oxygen.}}{\mathrm{O_2}}$$

The nitric constituents of the salt may be partially economized by previously thoroughly mixing with the dry mercuric nitrate as much mercury as is used in its preparation, or as much as it already contains (ascertained by calculation from the atomic weights and the weight of nitrate under operation, as in making mercurous sulphate), and well heating the mixture. In this case the free mercury is also converted into mercuric oxide. This is the official process, the pharmacopœial quantities being four ounces of mercury dissolved in four and a half fluid ounces of nitric acid diluted with two ounces of water, the solution evaporated to dryness, the residue thoroughly mixed with four more ounces of mercury, and the whole heated until acid vapours cease to be evolved. (Mercuric oxide is tested for nitrate by heating a little of the sample in a test-tube, when orange nitrous vapours are produced and are visible in the upper part of the tube, if nitrate be present.)

$$\underset{\text{Mercuric nitrate.}}{Hg2NO_3} \quad + \quad \underset{\text{Mercury.}}{Hg} \quad = \quad \underset{\text{Mercuric oxide.}}{2HgO} \quad + \quad \underset{\text{Nitric peroxide.}}{2NO_2}$$

Mercuric oxide is an orange-red powder, more or less crystalline according to the extent to which it may have been stirred during preparation from the nitrate, much rubbing giving it a pulverulent character. Mixed with hard and soft paraffin, it yields the *Unguentum Hydrargyri Oxidi Rubri*, B.P. (1 part in 8). Mercuric oxide, in contact with oxidizable organic matter, is liable to reduction to black or mercurous oxide.

Ninth Synthetical Reaction.—To solution of potash, or soda, or lime-water, in a test-tube or larger vessel, ad solution of corrosive sublimate or of mercuric nitrate; yellow oxide of mercury, or yellow mercuric oxide (HgO), is precipitated (*Hydrargyri Oxidum Flavum*, B.P.).

$$\underset{\substack{\text{Mercuric}\\ \text{chloride.}}}{HgCl_2} \quad + \quad \underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{Ca2HO} \quad = \quad \underset{\substack{\text{Mercuric}\\ \text{oxide.}}}{HgO} \quad + \quad \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{CaCl_2} \quad + \quad \underset{\text{Water.}}{H_2O}$$

Eighteen grains of corrosive sublimate to ten ounces of lime-water form the *Lotio Hydrargyri Flava*, B.P. The precipitate only differs physically from the red mercuric oxide; the yellow is more minutely divided than the red. Mercuric oxide is very slightly soluble in water, but sufficiently so to communicate a metallic taste.

Tenth Synthetical Reaction.—To calomel add solution of potash or soda, or lime-water; black oxide of mercury, or mercurous oxide (Hg_2O), is produced, and may be filtered off, washed and dried. (This reaction and the formation of a white curdy precipitate, on the addition of solution of nitrate of silver to the filtrate from the mercurous oxide, acidified by nitric acid, form sufficient evidence of a powder being or containing calomel. The curdy precipitate is chloride of silver.)

Thirty grains of calomel to ten ounces of lime-water form the *Lotio Hydrargyri Nigra*, B.P.

$$\underset{\substack{\text{Mercurous}\\\text{chloride.}}}{2HgCl} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Mercurous}\\\text{oxide.}}}{Hg_2O} + \underset{\substack{\text{Chloride of}\\\text{calcium.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

Reactions having Analytical Interest (Tests).

(The mercury occurring as mercuric or mercurous salt.)

First Analytical Reaction.—The Copper Test. Deposition of mercury upon and sublimation from copper.—Place a small piece of bright copper, about half an inch long and a quarter of an inch broad, in a solution of any salt of mercury, mercurous or mercuric, and heat in a test-tube; the copper becomes coated with mercury in a fine state of division. (The absence of any notable quantity of nitric acid must be ensured, or the copper itself will be dissolved. *See* below.) Pour away the supernatant liquid from the copper, wash the latter once or twice by pouring water into, and then out of, the tube, remove the metal, take off excess of water by gentle pressure in a piece of filter-paper, dry the copper by passing it quickly through a flame, holding it by the fingers; finally, place the copper in a dry, narrow test-tube, and heat to redness in a flame, the tube being held almost horizontally; the mercury sublimes and condenses as a whitish sublimate of minute globules on the cool part of the tube outside the flame. The globules aggregate on gently pressing with a glass rod, and are especially visible where flattened between the rod and the side of the test-tube.

Notes on the Test.—This is a valuable test for several reasons:—It is very delicate when performed with care. It brings before the observer the element itself—one which, from its metallic lustre and fluidity, cannot be mistaken for any other. It is a test for mercurous and mercuric salts. It eliminates mercury in the presence of most other substances, organic or inorganic.

In performing the test, the presence of any quantity of nitric acid may be avoided by adding an alkali until a slight permanent precipitate appears, and then very slightly re-acidifying with a drop or two of acetic acid; or by concentrating in an evaporating-dish after adding a little sulphuric acid, and then rediluting.

Tests continued. Mercuric salts.

Second Analytical Reaction.—To a few drops of a solution of a mercuric salt (corrosive sublimate, for example) add solution of iodide of potassium, drop by drop; a yellowish-red precipitate (mercuric iodide, HgI_2) forms, and at first redissolves, but is permanent when sufficient iodide of potassium has been added. Continue the addition of iodide of potassium; the precipitate is redissolved. (*See* Notes on p. 226.)

Third Analytical Reaction.—Add a solution of mercuric salt to solution of ammonia, taking care that the mixture, after well stirring, still smells of ammonia; a white precipitate falls.

Ammoniated Mercury.

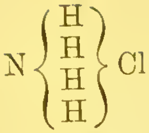
Performed in a test-tube, this reaction is a very delicate test of the presence of a mercuric salt; performed in larger vessels, the mercuric salt being corrosive sublimate (3 ounces dissolved in 3 pints of distilled water, the solution poured into 4 fluid ounces of Solution of Ammonia, and the precipitate washed and dried over a water-bath), it is the usual and the pharmacopœial process for the preparation of "white precipitate," the old "ammonio-chloride" or "amido-chloride of mercury" (so-called because then considered to be a compound of mercury with chlorine and with *amidogen*, NH_2, or $HgCl_2Hg2NH_2$, chloride and *amide* of mercury), now known as Ammoniated Mercury (*Hydrargyrum Ammoniatum*, B.P.).

Constitution of Ammoniated Mercury.—This precipitate is now, however, considered to be the chloride of mercuric-ammonium ($NH_2Hg'Cl$)—that is, chloride of ammonium (NH_4Cl) in one molecule of which two univalent atoms of hydrogen are substituted by one bivalent atom of mercury.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Ammonia.}}{2NH_4HO} = \underset{\text{“White precipitate.”}}{NH_2Hg''Cl} + \underset{\text{Chloride of ammonium.}}{NH_4Cl} + \underset{\text{Water.}}{2H_2O}$$

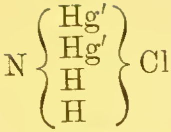
Varieties of Ammoniated Mercury.—If the order of mixing be reversed, and ammonia be added to solution of mercuric chloride, a double chloride of mercuric-ammonium and mercury results ($NH_2HgCl,HgCl_2$): it contains 76·55 per cent. of mercury. Previously to the year 1826, "white precipitate" was officially made by adding a fixed alkali to a solution of equal parts of corrosive sublimate and sal-ammoniac; this gave a double chloride of mercuric-ammonium and ammonium (NH_2HgCl,NH_4Cl), containing 65·57 per cent. of mercury. This compound is now known as "*fusible* white precipitate," because at a temperature somewhat below redness it fuses and then volatilizes. The "white precipitate," which has been official since 1826, contains, theoretically, 79·52 per cent. of mercury. The true compound may be distinguished as "*infusible* white precipitate," from the fact that when heated it volatilizes without fusing. An ointment of this body is official (*Unguentum Hydrargyri Ammoniati*, B.P.). Prolonged washing with water converts "white precipitate" into a yellowish compound (NH_2HgCl,HgO); hence the official preparation is not thoroughly freed from the chloride of ammonium which is formed during its manufacture, but which, if present in larger proportion than seven or eight per cent., gives to it the character of partial or complete fusibility. The officially recognised "ammoniated mercury" should volatilize at a temperature below redness without fusing, and should yield 77·5 per cent. of metallic mercury. With iodine, chlorine, or bromine, white precipitate may yield the highly and dangerously explosive iodide, chloride, or bromide of nitrogen.

Note.—Chloride of mercuric-ammonium is only one member of a large class of compounds derivable from the various salts of ammonium by substitution of atoms of hydrogen in the molecules by atoms of other radicals. The composition of the chloride of mercurous-ammonium (*see* page 238) and of ammonio-nitrate of silver (B.P.) is consistent with this view. In these formulæ ammonium is symbolized by NH_4 or Am, indifferently. The use of the latter promotes clearness in the formulæ, but it must only be employed when the ammonium acts like an elementary radical.



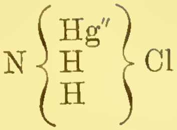
$$\mathrm{N}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Cl}$$

Chloride of (common) ammonium.



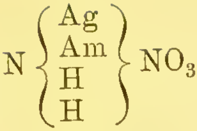
$$\mathrm{N}\left\{\begin{matrix}\mathrm{Hg'}\\\mathrm{Hg'}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Cl}$$

Chloride of mercurous-ammonium.



$$\mathrm{N}\left\{\begin{matrix}\mathrm{Hg''}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Cl}$$

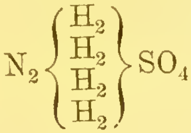
Chloride of mercuric ammonium.



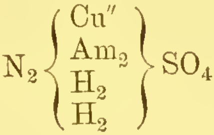
$$\mathrm{N}\left\{\begin{matrix}\mathrm{Ag}\\\mathrm{Am}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{NO_3}$$

Nitrate of argent-ammon-ammonium.

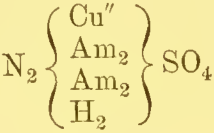
The composition of the ammonio-sulphates of copper (pp. 200 and 219) is consistent with the second and third of the following formulæ, the first being that of sulphate of ammonium:—



$$\mathrm{N_2}\left\{\begin{matrix}\mathrm{H_2}\\\mathrm{H_2}\\\mathrm{H_2}\\\mathrm{H_2}\end{matrix}\right\}\mathrm{SO_4}$$



$$\mathrm{N_2}\left\{\begin{matrix}\mathrm{Cu''}\\\mathrm{Am_2}\\\mathrm{H_2}\\\mathrm{H_2}\end{matrix}\right\}\mathrm{SO_4}$$



$$\mathrm{N_2}\left\{\begin{matrix}\mathrm{Cu''}\\\mathrm{Am_2}\\\mathrm{Am_2}\\\mathrm{H_2}\end{matrix}\right\}\mathrm{SO_4}$$

The iodide of dimercuric-ammonium (NHg''_2I) is formed in testing for ammonia by the "Nessler" reagent (*vide* Index). Troost has obtained $NHAm_3Cl$.

Fourth Analytical Reaction.—Pass sulphuretted hydrogen through a mercuric solution; a black precipitate (mercuric sulphide, HgS) falls.

Note.—Sulphuretted hydrogen also precipitates mercurous sulphide (Hg_2S) from mercurous solutions; and in appearance the precipitates are alike; hence this reagent does not distinguish between mercurous and mercuric salts. But in the course of systematic analysis, mercuric salts are thrown down from solution as sulphide after mercurous salts have been otherwise removed. Both sulphides are insoluble in sulphydrate of ammonium.

Note.—An insufficiency of gas gives a white or coloured precipitate of oxysulphide. Prolonged contact with sulphuretted hydrogen or a sulphydrate, especially if warm, converts the black into a red sulphide.

Ethiop's Mineral, the old *Hydrargyri Sulphuretum cum Sulphure*, is a mixture of sulphide of mercury and sulphur, obtained on triturating the elements in a mortar till globules are no longer visible. Its name is probably in allusion to its similarity in colour to the skin of the Æthiop.

Vermilion is mercuric sulphide prepared by sublimation. For a description of the Chinese method of manufacturing it, see the *Pharmaceutical Journal* for December 17th, 1881.

Tests continued. Mercurous salts.

Fifth Analytical Reaction.—To a solution of a mercurous salt (the mercurous nitrate obtained in the second synthetical reaction, for example) add hydrochloric acid or any soluble chloride ; a white precipitate (calomel, HgCl) occurs. This reaction was formerly official in the Dublin Pharmacopœia as a process for the preparation of calomel.

Sixth Analytical Reaction.—To solution of a mercurous salt add iodide of potassium; a green precipitate results (mercurous iodide, HgI).

Seventh Analytical Reaction.—To a mercurous salt, dissolved or undissolved (*e.g.* calomel), add ammonia; a black salt (*e.g.* chloride) of mercurous-ammonium (NH_2Hg_2Cl) is formed. (See page 236 for explanation of composition.)

Other Tests for Mercury.

The elimination of mercury in the actual state of metal by the copper test, coupled with the production or non-production of a white precipitate on the addition of hydrochloric acid to the original solution, is usually sufficient evidence of the presence of mercury and its existence as a mercurous or mercuric salt. But other tests may sometimes be applied with advantage. Thus metallic mercury is deposited on placing a drop of the solution on a plate of gold (sovereign or half-sovereign), and touching the drop and the edge of the plate simultaneously with a key: an electric current passes, under these circumstances, from the gold to the key, and thence through the liquid to the gold, decomposing the salt, the mercury of which forms a white metallic spot on the gold, while the other elements go to the iron. This is called the *galvanic test*, and is useful for clinical purposes.—Solution of stannous chloride ($SnCl_2$)—*see* Index,—from the readiness with which it forms stannic salts ($SnCl_4$, SnO_2, etc.), gives a white precipitate of mercurous chloride in mercuric solutions, and quickly still further reduces this mercurous chloride (and other mercury salts) to a greyish mass of finely divided mercury; this is the old *magpie test*, probably so called from the white and grey appearance of the precipitate. The reaction may even be obtained from such insoluble mercury compounds as "white precipitate." ——Confirmatory tests for mercuric and mercurous salts will be found in the action of solution of potash, solution of soda, lime-water, solution of ammonia and solution of iodide of potassium. (*Vide* pages 233, 235, and 238.)——Normal alkaline carbonates produce yellowish mercurous carbonate and brownish-red mercuric carbonate, both of them unstable. ——Alkaline bicarbonates give yellowish mercurous carbonate with mercurous solutions, and with mercuric salts, white (becoming red) mercuric oxysalt.——Yellow chromate of potassium (K_2CrO_4) gives, with mercurous salts, a red precipitate (mercurous chromate, Hg_2CrO_4).——Mercury and all its compounds are volatile, many of them being decomposed at the same time, and yielding globules of condensed metal; the experiment is most conveniently performed in a test-tube.——All dry compounds of mercury are decomposed when heated in a dry test-tube with dried carbonate of sodium, mercury subliming and condensing in visible globules, or as a whitish deposit, yielding globules when rubbed with a glass rod.

Antidote.—Albumen gives a white precipitate with solution of mercuric salts; hence the importance of administering white of egg, while waiting for a stomach-pump or stomach-siphon, in case of poisoning by corrosive sublimate.

QUESTIONS AND EXERCISES.

Name the chief ore of mercury, and describe a process for the extraction of the metal.—Give the properties of mercury.—In what state does mercury exist in "Grey Powder"?—What other preparations of metallic mercury itself are employed in medicine?—State the relation of the mercurous to the mercuric compounds.—Distinguish between an *alloy* and an *amalgam*.—State the formulæ of the two Iodides of Mercury.—Under what circumstances has mercuric iodide different colours?—Illustrate the chemical law of Multiple Proportions as explained by the atomic theory, employing for that purpose the stated composition of the two iodides of mercury.—Write down the formulæ of Mercurous and Mercuric Nitrates and Sulphates.—How is Mercuric Sulphate prepared?—What is the formula of "Turpeth Mineral"?—Describe the processes necessary for the conversion of mercury into Calomel and Corrosive Sublimate, using diagrams.—Why is black oxide of manganese sometimes mixed with the other ingredients in the preparation of corrosive sublimate?—Give the chemical and physical points of difference between calomel and corrosive sublimate.—How may calomel in corrosive sublimate be detected?—Work out a sum showing how much Mercury will be required in the manufacture of one ton of Calomel. *Ans.*, 17 cwt. nearly.—Mention the official preparations of the Chlorides of Mercury.—Give the formulæ and mode of formation of the Red, Yellow, and Black Oxides of Mercury, employing diagrams.—Explain the action of the chief general test for Mercury.—How are mercurous and mercuric salts analytically distinguished?—Give a probable view of the constitution of *Hydrargyrum Ammoniatum*, B.P., and an equation showing how it is made.—State the best temporary antidote to poisoning by mercury?

LEAD.

Symbol, Pb. Atomic weight, 206·4.

Source.—The ores of lead are numerous; but the one from which the metal is chiefly obtained is the sulphide of lead (PbS), or *galena* (from γαλήνη, *galēnē*, tranquillity, perhaps from its supposed effect in allaying pain).

Preparation.—The ore is first roasted in a current of air; much sulphur is thus burnt off as sulphurous acid gas, while some of the metal is converted into oxide and a portion of the sulphide oxidized to sulphate. Oxidation being stopped when the mass presents certain appearances, the temperature is raised, and the oxide and sulphate, reacting on undecomposed sulphide, yield the metal and much sulphurous acid gas:—$2PbO + PbS = Pb_3 + SO_2$ and $PbSO_4 + PbS = Pb_2 + 2SO_2$.

Uses.—The uses of lead are well known. Alloyed with some arsenium, it forms common *shot*, with antimony gives *type-metal*, with tin *solder*, and in smaller quantities enters into the composition of *Britannia metal*, *pewter*, and other alloys. Lead is so slightly attacked by acids that chemical vessels and instruments are sometimes made of it. Hot hydrochloric acid slowly converts it into chloride of lead with evolution of hydrogen. Sulphuric acid by aid of air only very slightly attacks it with formation of sulphate of lead and water.

Even nitric acid very slowly converts it into nitrate with evolution of nitric oxide and nitrous oxide gases and water.

The salts of lead used in pharmacy and all other preparations of lead are obtained, directly or indirectly, from the metal itself. Heated in a current of air, lead combines with oxygen and forms oxide of lead (PbO), a yellow powder (*massicot*), or, if fused and solidified, a brighter, reddish-yellow, heavy mass of bright scales (*Plumbi Oxidum*, B.P.), termed *litharge* (from λίθος, *lithos*, a stone, and ἄργυρος, *arguros*, silver). It is from this oxide that the chief lead compounds are obtained. Oxide of lead, by further roasting in a current of air, yields *red lead* (or *minium*), Pb_3O_4, or $PbO_2 2PbO$. Both oxides are much used by painters, paper-stainers, and glass-manufacturers. *White lead* is a mixture of carbonate ($PbCO_3$) and hydrate of lead ($Pb2HO$) (commonly 2 molecules of the former to 1 of the latter), usually ground up with about 7 per cent. of linseed-oil; it is made by exposing lead, cast in spirals or little gratings, to the action of air, acetic fumes, and carbonic acid gas, the latter generated from decaying vegetable matter, such as spent tan: oxyacetate of lead slowly but continuously forms, and is as continuously decomposed by the carbonic acid gas with production of hydrate and carbonate, or *dry white lead.* The grating-like masses, when ground, form the heavy white pulverulent official *Plumbi Carbonas*, B.P. The latter is the active constituent of *Unguentum Plumbi Carbonatis*, B.P., the old *Unguentum Cerussæ.* It is also made by bringing carbonic acid gas and litharge together in a solution of acetate of lead.

Lead compounds are poisonous, producing saturnine colic, and even paralysis. These effects are termed *saturnine* from an old name of lead, *Saturn.* The alchemists called lead Saturn, first, because they thought it the oldest of the seven then known metals, and it might therefore be compared to Saturn, who was supposed to be the father of the gods; and, secondly, because its power of dissolving other metals recalled a peculiarity of Saturn, who was said to be in the habit of devouring his own children.

Quantivalence.—The atom of lead is sometimes quadrivalent (Pb''''); but in most of the compounds used in medicine it exerts bivalent activity only (Pb'').

REACTIONS HAVING SYNTHETICAL INTEREST.

Acetate of Lead.

First Synthetical Reaction.—Place a few grains of oxide of lead in a test-tube, add about an equal weight of water and two and a half times its weight of acetic acid, and boil; the oxide dissolves (or, rather, disappears—dissolves with simultaneous decomposition) and forms a solution of acetate of lead ($Pb2C_2H_3O_2$). When cold, or on evaporation, if much water has been used (the solution being kept faintly acid), crystals of acetate of lead ($Pb2C_2H_3O_2, 3H_2O$) are deposited. Larger quantities are obtained by the same method.

$$\underset{\text{Oxide of lead.}}{PbO} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Acetate of lead.}}{Pb2C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

This is the official process for *Plumbi Acetas*, B.P. The salt is termed *Sugar of Lead*, from its sweet taste. Besides its direct use in pharmacy, it forms three-fourths of the *Pilula Plumbi cum Opio*, B.P., is the chief constituent of *Unguentum Plumbi Acetatis*, B.P., and an ingredient in *Suppositoria Plumbi Composita*, B.P.

Subacetate or Oxyacetate of Lead.

Second Synthetical Reaction.—Boil acetate of lead with four times its weight of water and rather more than two-thirds its weight of oxide of lead; the filtered liquor is solution of oxyacetate of lead, *Liquor Plumbi Subacetatis*, B.P.

The official *Liquor* is made by boiling 5 ounces of acetate and 3½ of oxide in one pint of distilled water for half an hour (constantly stirring), filtering, and making up for any loss due to evaporation by diluting the filtrate to 1 pint. It contains about 24 per cent. of the oxyacetate of lead, $Pb_2O2C_2H_3O_2$.

A similar solution was used by M. Goulard, who called it *Extractum Saturni*, and drew attention to it in 1770. It is now frequently termed *Goulard's Extract*. A more dilute solution, 1 of *Liquor* and 1 of spirit in 80 of *distilled* water, is also official in the British Pharmacopœia, under the name of *Liquor Plumbi Subacetatis Dilutus*. The latter is commonly known as *Goulard Water.* A strong solution of oxyacetate of lead in glycerine constitutes the *Glycerinum Plumbi Subacetatis*, B.P., and this with a mixture of soft and hard paraffin gives the *Unguentum Glycerini Plumbi Subacetatis*, B.P., a modification of the old *Goulard's Cerate.*

Oxyacetates of lead.—The official "subacetate of lead" is not a definite chemical salt. It is probably a mixture of two subacetates of lead, which are well-known crystalline compounds, and which the author is disposed to regard as having a constitution similar to that he has already indicated for some other salts (*see* Iron and Antimony, also Bismuth). Exposed to air, it absorbs carbonic acid gas, and hydratocarbonate of lead is deposited.

	Acetate of lead (3 molecules) . .	$Pb_36C_2H_3O_2$
B.P.	Pyro-oxyacetate of lead	$Pb_3O4C_2H_3O_2$
	Goulard's oxyacetate of lead. . .	$Pb_3O_22C_2H_3O_2$
	Oxide of lead (3 molecules) . . .	Pb_3O_3

$$\underset{\text{Oxide of lead.}}{PbO} + \underset{\text{Acetate of lead.}}{Pb2C_2H_3O_2} = \underset{\text{Official "subacetate."}}{Pb_2O2C_2H_3O_2}$$

$$\text{or } \underset{\text{Oxide of lead.}}{3PbO} + \underset{\text{Acetate of lead.}}{3(Pb2C_2H_3O_2)} = \underset{\text{The official "subacetate."}}{\underset{\text{Pyro-oxyacetate.}}{Pb_3O4C_2H_3O_2} + \underset{\text{Goulard's oxyacetate.}}{Pb_3O_22C_2H_3O_2}}$$

Nitrate of Lead. Red Lead. Peroxide of Lead.

Third Synthetical Reaction.—Digest a few grains of red lead in nitric acid and water; nitrate of lead ($Pb2NO_3$) is formed, and remains in solution, while a puce-coloured peroxide of lead (PbO_2) is precipitated. The *Nitrate of Lead* (*Plumbi Nitras*, B.P.) is more directly made by dissolving litharge (PbO) in nitric acid.

$$PbO + 2HNO_3 = Pb2NO_3 + H_2O.$$

The former reaction serves to bring before the student two other oxides of lead, namely, red lead (Pb_3O_4) and peroxide of lead (PbO_2). In the latter oxide the quadrivalent character of lead is obvious. Nitrate of lead is used officially in preparing iodide of lead. For the latter purpose the above mixture may be filtered, the precipitate of peroxide of lead purified from adhering nitrate by passing hot water through the filter, the filtrate and washings evaporated to dryness to remove excess of nitric acid, the residual nitrate of lead redissolved by ebullition with a small quantity of hot water, and the solution set aside to crystallize or a portion at once used for the following experiment. Nitrate of lead forms white crystals derived from octahedra.

Peroxide of lead dissolved in cold strong hydrochloric acid apparently yields an unstable perchloride ($PbCl_4$).

Iodide of Lead.

Fourth Synthetical Reaction.—To a neutral solution of nitrate of lead add solution of iodide of potassium; a precipitate of iodide of lead (PbI_2) falls (*Plumbi Iodidum*, B.P.). Equal weights of the salts may be used in making large quantities.

$$\underset{\text{Nitrate of lead.}}{Pb2NO_3} + \underset{\text{Iodide of potassium.}}{2KI} = \underset{\text{Iodide of lead.}}{PbI_2} + \underset{\text{Nitrate of potassium.}}{2KNO_3}$$

Iodide of lead is the chief ingredient in *Emplastrum Plumbi Iodidi*, B.P., and *Unguentum Plumbi Iodidi*, B.P. Iodide of lead is soluble in solution of chloride of ammonium.

Crystals of Iodide of Lead.—Heat the iodide of lead with the supernatant liquid, and, if necessary, filter; the salt is dissolved, and again separates in golden crystalline scales as the solution cools.

Oleate of Lead. (Lead Plaster.)

Fifth Synthetical Reaction.—Boil together in a small dish a few grains of very finely powdered oxide of lead, with twice its weight of olive-oil, and two or three times as much water, well stirring the mixture, and from time to time replacing water that has evaporated; the product is a white mass of oleate of lead ($Pb2C_{18}H_{33}O_2$) (*Emplastrum Plumbi*. B.P.), glycerine remaining in solution. Larger quantities are prepared in the same manner.

$$\underset{\text{Oxide of lead.}}{3PbO} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Oleate of glyceryl (olive-oil or oleine).}}{2(C_3H_53C_{18}H_{33}O_2)}$$

$$= \underset{\text{Oleate of lead (lead plaster).}}{3(Pb2C_{18}H_{33}O_2)} + \underset{\text{Hydrate of glyceryl (glycerine).}}{2(C_3H_53HO)}$$

The action between the oxide of lead and olive-oil is slow, requiring several hours for its completion. Lead plaster is a constituent of eleven of the fourteen plasters (*Emplastra*) mentioned in the British Pharmacopœia.

The *glycerine* may be obtained by treating the aqueous product of the above reaction with sulphuretted hydrogen to remove a trace of lead, then digesting with animal charcoal, filtering, and evaporating. But on the large scale glycerine is produced as a by-product in the manufacture of candles; for its elements are found in nearly all vegetable and animal fats. (*Vide* Index.) If in making lead plaster the mixture be evaporated to dryness, some of the glycerine will escape with the steam and some remain with the plaster.

Modes of formation of *Chloride*, *Sulphide*, *Chromate*, *Sulphate*, *Hydrate*, and other salts of lead are incidentally described in the following analytical paragraphs.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—To solution of a lead salt (acetate, for example) add hydrochloric acid; a white precipitate (chloride of lead, $PbCl_2$) is obtained. Boil the precipitate with much water; it dissolves, but, on the solution cooling, is redeposited in small acicular crystals. Filter the cold solution, and pass sulphuretted hydrogen through it; a black precipitate (sulphide of lead, PbS) shows that the chloride of lead is soluble to a slight extent in cold water.

Note.—A white precipitate on the addition of hydrochloric acid, soluble in hot water, and blackened by sulphuretted hydrogen, sufficiently distinguishes lead salts from those of other metals; but the non-production of such a precipitate does not prove the absence of a small quantity of lead, chloride of lead being slightly soluble in cold water.

Second Analytical Reaction.—Through a dilute solution of a lead salt, acidulated with hydrochloric acid, pass sulphuretted hydrogen; a black precipitate (sulphide of lead, PbS) occurs.

Lead in Water.—The foregoing is a very delicate test. Should a trace of lead be present in water used for drinking purposes, sulphuretted hydrogen will detect it. On passing the gas through a pint of such (acidulated) water, a brownish colour is produced. If the tint is scarcely perceptible, set the liquid aside for a day; the gas will become decomposed and a thin layer of sulphur be found at the bottom of the vessel, white if no lead be present, but more or less brown if it contain sulphide of lead. Hygienists regard one-twentieth of a grain of lead per gallon as dangerous, while a lesser quantity may do harm. Water commonly used for drinking purposes should not contain a trace.

Third Analytical Reaction.—To solution of a lead salt add sulphydrate of ammonium; a black precipitate (sulphide of lead) falls, insoluble in excess.

Fourth Analytical Reaction.—To solution of a lead salt add solution of chromate of potassium (K_2CrO_4); a yellow precipitate (chromate of lead, $PbCrO_4$) is formed, insoluble in weak acids or in solution of chloride of ammonium.

Chromes.—This reaction has technical as well as analytical interest. The precipitate is the common pigment termed *chrome yellow*, or *lemon chrome*. Boiled with lime and water, a portion of the chromic radical is removed as a soluble chromate of calcium, and an oxychromate of lead, of a bright red or orange colour (*orange chrome*), is produced.

Fifth Analytical Reaction.—To solution of a lead salt add dilute sulphuric acid, or solution of a sulphate; a white precipitate (sulphate of lead, $PbSO_4$) falls.

Sulphate of lead is slightly soluble in strong acids, and in solutions of alkaline salts; it is insoluble in acetic acid. It is readily dissolved and, indeed, decomposed by solution of acetate of ammonium, the liquid yielding the ordinary reactions with soluble chromates and iodides.

In dilute solutions the above sulphuric reaction does not take place immediately; the precipitate, however, falls after a time; its appearance may be hastened by evaporating the mixture nearly to dryness and then rediluting.

The white procipitate generally noticed in the vessels in which diluted sulphuric acid is kept is sulphate of lead, derived from the leaden chambers in which the acid is made: solubility in strong acid and insolubility in weak explains its appearanco.

Antidotes.—From the insolubility of sulphate of lead in water, the best *antidote*, in a case of poisoning by the acetate or other soluble salt of lead, is a soluble sulphate, such as Epsom salt, sulphate of sodium, or alum, vomiting being also induced or the stomach-pump, or stomach-siphon, applied as quickly as possible.

Other tests for lead will be found in the reaction with *iodide of potassium* (*vide* p. 244); with *alkaline carbonates*, a white precipitate ($2PbCO_3 + Pb2HO$) insoluble in excess; with *alkalies*, a white precipitate ($Pb2HO$) more or less soluble in excess; with alkaline *phosphates*, *arseniates*, *ferrocyanides* and *cyanides*, precipitates mostly insoluble, but of no special analytical interest. Insoluble salts of lead may be decomposed by solution of potash (KHO) or soda ($NaHO$).

The metal is precipitated in a beautifully crystalline state by metallic zinc and some other metals; the *lead tree* is thus formed.——The *blowpipe-flame* decomposes solid lead compounds placed in a small cavity in a piece of charcoal, a soft malleable bead of metal being produced, and a yellowish ring of oxide deposited on the charcoal.

QUESTIONS AND EXERCISES.

Write down equations descriptive of the smelting of galena.—Mention some of the alloys of lead.—How is litharge produced?—Give the formulæ of white lead and red lead.—Describe the manufacture of white lead.—What is the quantivalence of lead?—Draw a diagram showing the formation of Acetate of Lead.—Describe the preparation and composition of *Liquor Plumbi Subacetatis*, B.P.—What is the action of nitric acid on red lead, litharge, and lead?—How is the official Iodide of Lead prepared?—Describe the reaction between oxide of lead, water, and olive-oil, at the temperature of boiling water, and give chemical formulæ explanatory of the constitution of the products.—Mention the chief tests for lead.—How would you search for lead in potable water?—What is the composition of chrome yellow?—State a method whereby lead, barium, and silver, in solution, may be separated from each other.—Name the best antidote in cases of poisoning by salts of lead.

SILVER.

Symbol, Ag. Atomic weight, 108.

Source.—This element occurs in Nature in the metallic state and as ore, the common variety of the latter being sulphide of silver (Ag_2S) in combination with much sulphide of lead, forming *argentiferous galena*.

Preparation.—The lead from such galena (p. 240) is melted and slowly cooled; crystals of lead separate and are raked out from the still fluid mass, and thus an alloy very rich in silver is finally obtained; this is roasted in a current of air, whereby the lead is oxidized and removed as litharge, pure silver remaining. Other ores undergo various preparatory treatments according to their nature, and are then shaken with mercury, which amalgamates with and dissolves the particles of metallic silver, the mercury being subsequently removed from the amalgam by distillation. Soils and minerals containing metallic silver are also treated in this way. An important improvement in the amalgamation process, by which the mercury more readily unites with the silver, consists in the addition of a small proportion of sodium to the mercury. Chloride of silver may be dissolved from ores by solution of hyposulphite of sodium.

Silver is not readily affected by the weak acid or other fluids of food, though it is rapidly tarnished by sulphur or sulphur compounds. It does not perceptibly attack hydrochloric acid; reduces strong nitric acid to nitrous anhydride (N_2O_3), and a weaker acid to nitric oxide (NO); it reduces hot sulphuric acid to sulphurous anhydride (SO_2), sulphate of silver (Ag_2SO_4) being formed. The latter salt is crystalline, and slightly soluble in water.

REACTIONS HAVING SYNTHETICAL INTEREST.

Impure Nitrate of Silver.

First Synthetical Reaction.—Dissolve a silver coin in nitric acid; nitric oxide gas (NO) and nitrous anhydride (N_2O_3) are evolved, and a solution of nitrates of silver and copper is obtained.

Silver Coinage.—Pure silver is too soft for use as coin; it is therefore hardened by alloying with copper. The silver money of England contains 7·5, of Prussia 25, and of France 10 and 16·5 per cent. of copper—for the fineness of the French standard silver is 0·900 in the five-franc piece, while an inferior alloy of 0·835 is used for the lower denominations. The single-franc piece, composed of the latter alloy, is still made to weigh five grammes, the weight originally chosen for the franc as the unit of the monetary scale when the fineness of the coin was 0·900. It has now become a token, like the British shilling, of which the nominal value exceeds the metallic value. One pound troy of British standard silver is coined into 66 shillings, of which the metal is worth from 50*s.* to 60*s.*, or less or more, according to the market price of silver. The standard fineness of this silver is 0·925, *i.e.* 3 of copper in 40 of the alloy. British silver coins are a legal tender in payments to the amount of 40*s.* only.

Chloride of Silver.

Second Synthetical Reaction.—To the product of the foregoing reaction add water and hydrochloric acid or a soluble chloride; white chloride of silver ($AgCl$) is precipitated, copper still remaining in solution. Collect the precipitate on a filter and wash with water; it is pure chloride of silver.

Note.—Copper may also be separated by evaporating the solution of the metals in nitric acid to dryness and gently heating the residue, when the nitrate of copper is decomposed but the nitrate of silver is unaffected. The latter may be dissolved from the residual oxide of copper by water.

Chloride of silver may be obtained in crystals by evaporation of its solution in ammonia.

Pure Silver.

Third Synthetical Reaction.—Place the chloride of silver of the previous reaction in a dish, wet it with dilute sulphuric acid, and float a piece of sheet zinc on the mixture; metallic silver is precipitated, and after about one day wholly removed from combination. Collect the precipitate on a filter and wash with water; it is pure metallic silver, and is readily fusible into a single button, especially if mixed with a little borax and nitre.

Note.—Any considerable quantity of chloride of silver may be reduced to a lump of the metal by fusion, in a crucible, with about half its weight of carbonate of sodium. The chloride is also reduced by boiling with caustic alkali and grape sugar until a trial-sample is entirely dissolved by nitric acid.

Pure Nitrate of Silver.

Fourth Synthetical Reaction.—Dissolve the pure silver of the previous reaction in nitric acid (3 of silver require about 2 or 2½ of strong acid diluted with 5 of water), and remove excess of acid by evaporating the solution to dryness, slightly heating the residue; the product is pure nitrate of silver. Dissolve by heating with a small quantity of water; on the solution cooling, or on evaporation, colourless tabular crystals of nitrate of silver are obtained.

$$\underset{\text{Silver.}}{3Ag_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Nitrate of silver.}}{6AgNO_3} + \underset{\text{Water.}}{4H_2O}$$

Notes.—The solution of pure or refined silver (*Argentum Purificatum*, B.P.) in nitric acid, evaporation, and crystallization constitute the official process for the preparation of the nitrate (*Argenti Nitras*, B.P.). The salt, fused and poured into proper moulds, yields the white cylindrical sticks or rods commonly termed *caustic* (from καίω, *kaiō*, I burn), or *lunar caustic*. (The alchemists called silver *Diana* or *Luna*, from its supposed mysterious connection with the moon.) These "caustic points" often contain five per cent. of nitrate of potassium, which imparts toughness, the product being the officially recognised "Toughened Nitrate of Silver," or "Toughened Caustic." The "Nitrate of Silver and Potassium" (*Argenti et Potassii Nitras*, B.P.), or "Mitigated Caustic," is a fused mixture of one part of nitrate of silver with two parts of nitrate of potassium.

The specimen of nitrate of silver obtained in the foregoing reaction, dissolved in water, will be found useful as an analytical reagent. Nitrate of silver is soluble in rectified spirit; but after a time reaction and decomposition occur.

Silver salts are decomposed when in contact with organic matter, especially in the presence of light or heat, the metal itself being liberated, or a black insoluble compound formed. Hence the value of the nitrate in the manufacture of indelible ink for marking linen; hence, too, the reason of the practice of rendering silver solutions clear by subsidence and decantation, rather than by filtration through paper; and hence the cause of those cases of actual combustion which have been known to occur in preparing pills containing oxide of silver and essential oil or other organic matter. Linen marked with such ink should not be cleansed by aid of bleaching liquor, as the marked parts are then apt rapidly to be oxidized into perfectly rotten matter, holes resulting. Paul says the reaction is as follows:—$Ag_2O + CaCl_2O_2 = 2AgCl + CaO + O_2$.

Oxide of Silver.

Fifth Synthetical Reaction.—To solution of nitrate of silver add solution of potash or soda or lime-water; an olive-brown precipitate of oxide of silver (Ag_2O) occurs. The washed and dry oxide, like most silver compounds, is decomposed by heat with production of metal. It is also reduced by contact with organic matter. (*See* the previous paragraph.)

The *Argenti Oxidum*, B.P., is thus made, lime-water being the precipitant employed, soda or potash not being so readily removed by washing. Three and a half pints of good lime-water will decompose half an ounce of nitrate of silver.

$$\underset{\substack{\text{Nitrate of}\\\text{silver.}}}{2AgNO_3} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Oxide of}\\\text{silver.}}}{Ag_2O} + \underset{\substack{\text{Nitrate of}\\\text{calcium.}}}{Ca2NO_3} + \underset{\text{Water.}}{H_2O}.$$

Oxide of silver is also precipitated on adding ammonia to solution of nitrate of silver, but it rapidly is taken up by the nitrate of ammonium formed at the same time, nitrate of argentammonium, NH_3AgNO_3, being, doubtless, produced. More ammonia then yields nitrate of argentammon-ammonium (see p. 237). The direct solution of oxide of silver in ammonia may give the highly explosive substance known as Berthollet's fulminating silver (? NH_2Ag). Ordinary *fulminating silver*, $C_2N_2O_2Ag_2$, results from the interaction of nitrate of silver, nitric acid, and alcohol. The mercury compound, $C_2N_2O_2Hg$, is used in percussion caps.

Methods of forming several other salts of silver are incidentally mentioned in the following analytical paragraphs.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—To a solution of a silver salt add hydrochloric acid or other soluble chloride; a white curdy precipitate (chloride of silver) falls. Add nitric acid, and boil; the precipitate does not dissolve. Pour off the acid and add solution of ammonia; the precipitate dissolves. Neutralize the ammoniacal solution by an acid; the white curdy precipitate (chloride of silver, $AgCl$) is reproduced.

This is the most characteristic test for silver. The precipitated chloride is also soluble in solutions of hyposulphite of sodium or cyanide of potassium—facts of considerable importance in photographic operations.

Other analytical reagents than the above are occasionally useful.——Sulphuretted hydrogen, or sulphydrate of ammonium, gives a black precipitate (sulphide of silver, Ag_2S), insoluble in alkalies.——Solutions of potash or soda give a brown precipitate (oxide of silver, Ag_2O), converted into a fulminating compound by prolonged contact with ammonia. ——Phosphate of sodium gives a pale yellow precipitate (phosphate of silver, Ag_3PO_4), soluble in nitric acid and in ammonia.——Arseniate of ammonium gives a chocolate-coloured precipitate (arseniate of silver, Ag_3AsO_4), already noticed in connection with arsenic acid.——Iodide or bromide of potassium gives a yellowish-white precipitate (iodide or bromide of silver, AgI or $AgBr$), insoluble in acids and only slightly soluble in ammonia.——Cyanide of potassium gives a white precipitate (cyanide of silver, $AgCy$), soluble in excess, somewhat soluble in ammonia, insoluble in dilute nitric acid, soluble in boiling concentrated nitric acid.——Yellow chromate of potassium (K_2CrO_4) gives a red precipitate (chromate of silver, Ag_2CrO_4).——Red chromate of potassium also gives a red precipitate (acid chromate of silver, Ag_2CrO_4, CrO_3). ——Many organic acids afford insoluble salts of silver.—— Several metals displace silver from solution, mercury forming in this way a crystalline compound known as the silver tree, or *Arbor Dianæ.*——In the blowpipe-flame, silver salts, placed on charcoal with a little carbonate of sodium, yield bright globules of metal, accompanied by no incrustation as in the corresponding reaction with lead salts; the experiment may be performed with the nitrate, which first melts, and then, like all nitrates, deflagrates, yielding a white metallic coating of silver which slowly aggregates to a button.

Antidotes.—Solution of common salt, sal-ammoniac, or any other inert chloride should obviously be administered where large doses of nitrate of silver have been swallowed. A quantity of sea-water or brine would convert the silver into insoluble chloride, and at the same time produce vomiting.

DIRECTIONS FOR APPLYING SOME OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALS COPPER, MERCURY (MERCUROUS OR MERCURIC), LEAD, SILVER.

Add hydrochloric acid :—

Silver is indicated by a white curdy precipitate, soluble in ammonia.

Mercurous salts also by a white precipitate, turned black by ammonia.

Lead by a white precipitate, insoluble in ammonia. Confirm by boiling a small portion of the hydrochloric precipitate in water ; it dissolves.

If hydrochloric acid gives no precipitate, silver and mercurous salts are absent. Lead can only be present in very small quantity. Mercuric salts may be present. Copper may be present. Divide the liquid into three portions, and apply a direct test for each metal as follows :—

Lead is best detected by the sulphuric test, the tube being set aside for a time if the precipitate does not appear at once.

Mercury is best detected by the copper test. If present here, it occurs as mercuric salt.

Copper betrays itself by the blue colour of the liquid under examination. Confirm by the ammonia test.

If the above reactions are not thoroughly conclusive, confirmatory evidence should be obtained by the application of other reagents for copper, mercury, lead, or silver.

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALS COPPER, MERCURY (EITHER MERCUROUS OR MERCURIC SALT, OR BOTH), LEAD, SILVER.

Add hydrochloric acid, filter, and wash the precipitate with a small quantity of cold water.

<table>
<tr><td colspan="3">Ppt.
Pb Hg (ous) Ag.
Wash with boiling water.</td><td rowspan="3">Filtrate.
Cu Hg (ic) Pb.
Divide into three portions.
Test for
Cu by NH_4HO; blue sol.
Hg (mercuric) by Cu; globules.
Pb by H_2SO_4; white ppt.*</td></tr>
<tr><td colspan="2">Ppt.
Hg (ous) Ag.
Add NH_4HO.</td><td rowspan="2">Filtrate
Pb.
Add H_2SO_4,
white ppt.*</td></tr>
<tr><td>Precipitate
Hg
(mercurous),
black.</td><td>Filtrate
Ag.
Add an acid
white ppt.</td></tr>
</table>

OUTLINE OF THE FOLLOWING TABLES FOR ANY OR ALL OF THE COMMON METALS.

HCl	H_2S		NH_4HS	$(NH_4)_2CO_3$	$(NH_4)_2HAsO_4$	
Hg (as mercurous salt)	Cu	Insoluble in NH_4HS.	Zn	Ba	Mg	K
Pb (partially)	Hg (as mercuric salt)		Al	Ca		Na
Ag	Pb* (entirely)		Fe			NH_4
	As	Soluble in NH_4HS.				
	Sb					

The practical student should examine solutions containing these common metals until he is able to analyse with facility and accuracy. In this way he will best perceive the peculiarities of each element, and their general relations to each other. As the rarer metals are not included here, the Tables are not complete analytical schemes; only general memoranda respecting them will, therefore, now be given. For *complete* memoranda, see notes to subsequent complete Tables.

* Liquids containing only a small quantity of lead do not readily yield sulphate of lead on the addition of sulphuric acid. Before lead can be said to be absent, therefore, the liquid should be evaporated to dryness with one drop of sulphuric acid, and the residue digested in water; any sulphate of lead then remains as a heavy, white, insoluble powder.

MEMORANDA RELATING TO THE GENERAL ANALYTICAL TABLES FOR ANY OR ALL OF THE COMMON METALS (PAGE 257).

The group-reagents adopted in the Table are, obviously, *hydrochloric acid*, *sulphuretted hydrogen*, *sulphydrate of ammonium*, *carbonate of ammonium*, and *arseniate of ammonium*. If a group-reagent produces no precipitate, it is self-evident that there can be no member of the group present. At first, therefore, add only a small quantity of a group-reagent, and if it produces no effect add no more; for it is not advisable to overload a solution with useless reagents; substances expected to come down as precipitates are not infrequently held in the liquid by excess of acid, alkali, or strong aqueous solution of some group-reagent, thoughtlessly added. Indeed, experienced manipulators make preliminary trials with group-reagents on a few drops only of the liquid under examination; if a precipitate is produced, it is added to the bulk of the original liquid, and the addition of the group-reagent continued; if a precipitate is not produced, the few drops are thrown away, and the unnecessary addition of a group-reagent thus avoided altogether, an advantage fully making up for the extra trouble of making a preliminary trial.—While shunning excess, however, care must be taken to avoid deficiency; a substance only partially removed from solution through the addition of an insufficient amount of a reagent will appear where not expected, be constantly mistaken for something else, and cause much trouble; this will not occur if the appearance, odour, or reaction of the liquid on test-paper be duly observed. It is also a good plan, when

SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF ONE OF THE METALS HITHERTO CONSIDERED.

Add hydrochloric acid.

<table>
<tr>
<td rowspan="3">Ppt.
Hg(ous) Pb Ag
Add NH_4HO.
Hg(ous), black ppt.
Pb, ppt. still white.
Ag, ppt. dissolved.

Note 1.—If HCl gave no precipitate, neither Hg(ous) nor Ag is present; and Pb only in minute amount, if at all.
Note 2.—Hg obtained here must have existed in the solution as a mercurous salt.
Note 3.—Sb is also precipitated by HCl, but is dissolved on adding more HCl; the Hg, Pb, and Ag precipitates are not soluble in excess of HCl.</td>
<td colspan="3">If HCl gave no precipitate, the metal is still in the liquid; pass H_2S through it.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Cu Hg(ic) Pb As Sb.
As, yellow ppt.
Sb, orange ppt.
$\left.\begin{array}{l}\text{Cu}\\ \text{Hg(ic)}\\ \text{Pb}\end{array}\right\}$ black ppt.
Test original solution for Cu by NH_4HO; blue sol.
Hg by Cu; globules.
Pb by H_2SO_4; white ppt.

Note 1.—If H_2S gave no precipitate, neither Cu, Hg, Pb, As, nor Sb is present.
Note 2.—Hg and Pb may give coloured precipitates (oxysulphides) with H_2S if too little of the latter has been passed through the solution.</td>
<td colspan="2">If H_2S gave no precipitate, the metal is still in the liquid; add NH_4Cl, NH_4HO, and NH_4HS.</td>
</tr>
<tr>
<td>Ppt.
Fe Al Zn.
Fe, black ppt.
Test original solution for ferric salt by K_4Fcy (*dark* blue ppt.); and for ferrous salt by K_6Fdcy (*dark* blue ppt).
$\left.\begin{array}{l}\text{Al}\\ \text{Zn}\end{array}\right\}$ white ppt.
Test original solution by NH_4HO.
Al, white ppt, insoluble in excess.
Zn, white ppt. soluble in excess.</td>
<td>If NH_4HS, etc., gave no precipitate, the liquid may still contain either Ba, Ca, Mg, K, Na, or NH_4; add successively K_2CrO_4 for Ba, $Am_2C_2O_4$ for Ca, Na_2HPO_4 for Mg.
If neither Ba, Ca, nor Mg is found, examine the original solution for NH_4 by KHO, Na by the flame-test, and K by $PtCl_4$.</td>
</tr>
</table>

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF ORDINARY SALTS OF ANY OR ALL OF THE METALS HITHERTO CONSIDERED.

(READ THE "MEMORANDA" ON PAGE 255.)

Add hydrochloric acid, and filter.

<table>
<tr>
<td colspan="3">Precipitate
Hg(ous) Ag. Pb.
Wash, boil with water, filter.</td>
<td colspan="10">Filtrate
Cu Hg (ic) Pb As Sb Fe Al Zn Ba Ca Mg K Na NH_4.
Pass H_2S through the liquid until it ceases to cause any alteration; filter.</td>
</tr>
<tr>
<td colspan="2" rowspan="2">Precipitate
Hg(ous) Ag.
Add NH_4HO to the well-washed precipitate on the filter.</td>
<td rowspan="4">Filtrate
Pb.
Add H_2SO_4; white precipitate. (*See* footnote, p. 255.)</td>
<td colspan="3">Precipitate
Cu Hg(ic) Pb As Sb.
Wash, digest in NH_4HS, filter.</td>
<td colspan="7">Filtrate
Fe Al Zn Ba Ca Mg K Na NH_4.
Add NH_4HO, NH_4HS, and filter.</td>
</tr>
<tr>
<td rowspan="3">Precipitate
Cu Hg(ic) Pb.
Wash, dissolve in a few drops of HNO_3 and HCl; evap. nearly to dryness; redissolve in H_2O, divide into three, and test for
Cu by NH_4HO; blue solution.
Hg by Cu; globules.
Pb by H_2SO_4; white precip.</td>
<td colspan="2">Filtrate
As Sb.
Add $HC_2H_3O_2$, and boil; digest the precipitate in *strong* HCl; boil, dilute; filter.</td>
<td colspan="3">Precipitate
Fe Al Zn.
Wash, dissolve in HCl, boil (with a few drops of HNO_3 if necessary, p. 184); add KHO, stir, filter.</td>
<td colspan="4">Filtrate
Ba Ca Mg K Na NH_4.
Add $(NH_4)_2CO_3$; boil, filter.</td>
</tr>
<tr>
<td rowspan="2">Precip.
Hg(ous).
Black precipitate.</td>
<td rowspan="2">Filtrate
Ag.
Add HNO_3; white precipitate.</td>
<td>Precip.
As.
Yellow</td>
<td>Filtrate.
Sb.
Add H_2S. Orange precipitate.</td>
<td rowspan="2">Precipitate
Fe.
? Ferric or ferrous. Test original solution by yellow and red prussiates.</td>
<td colspan="2">Filtrate
Al Zn.
Neutralize by HCl; add NH_4HO, stir, fil.</td>
<td colspan="2">Precipitate
Ba Ca.
Wash, dissolve in $HC_2H_3O_2$, boil; add K_2CrO_4, filter.</td>
<td colspan="2">Filtrate
Mg K Na NH_4.
Add $(NH_4)_2HAsO_4$ stir, filter.</td>
</tr>
<tr>
<td colspan="2">Confirm by testing original solution by the H tests.</td>
<td>Precipitate
Al.
White precipitate.</td>
<td>Filtrate
Zn.
Add NH_4HS; white precipitate.</td>
<td>Precip.
Ba.
Yellow.</td>
<td>Filtrate.
Ca.
Add $(NH_4)_2C_2O_4$: white precipitate.</td>
<td>Ppt.
Mg.
White.</td>
<td>Filtrate
K Na NH_4.
Evap., ignite, dissol. in H_2O; test for K by $PtCl_4$; yel. ppt. Na by flame; yellow. NH_4 in orig. sol. by NaHO.</td>
</tr>
</table>

a group-reagent has produced a precipitate and the latter has been filtered out, to add a little more of the reagent to the clear filtrate; if more precipitate is produced, an insufficient amount of the group-reagent was introduced in the first instance; but the error is corrected by simply refiltering; if no precipitate occurs, the mind is satisfied and the way cleared for further operations.

Group-precipitates, or any precipitates still requiring examination, should, as a rule, be well washed before further testing; this is to remove the aqueous solution of other substances adhering to the precipitate (the mother-liquor as it is termed), so that subsequent reactions may take place fairly between the reagent used and the precipitate only.—A precipitate is sometimes in so fine a state of division as to retard filtration by clogging the pores of the paper, or even to pass through the filter altogether; in these cases the mixture may be warmed or boiled (or a fresh quantity of the original solution may be warmed *before* the group-reagent is added), which usually causes aggregation of the particles of a precipitate, and hence facilitates the passage of liquids.

Division of work.—It is immaterial whether a solution be first divided into group-precipitates or each precipitate be examined as soon as produced; if the former method be adopted, confusion will be avoided by labelling or marking the funnels or papers holding the precipitate "the HCl ppt.," "the H_2S ppt.," and so on.

The colours and general appearance of the various sulphides and hydrates precipitated should be borne in mind, as the absence of other bodies, as well as the presence of those thrown down, is often at once thus indicated.

Application of confirmatory tests must be frequent.

Results of analyses should be recorded neatly in a memorandum book; *a*, for correction and endorsement by the teacher; *b*, for future reference by the student, or, *c*, by those who may need evidence respecting his labours; and, *d*, promote mental orderliness.

The various reactions which occur in an analysis have already come before the reader in going through the tests for the individual metals or in other analytical operations; it is unnecessary, therefore, again to draw out equations or diagrams. But the reactions should be thought over, and if not perfectly clear to the mind, be written out again and again, till thoroughly understood.

QUESTIONS AND EXERCISES.

By what process is silver obtained from argentiferous galena?—What weight of English silver coin will yield one pound of pure nitrate of silver?—How may the metal be recovered from impure silver salts?—Give a diagram showing the formation of nitrate of silver.—Describe the reaction of lime-water and nitrate of silver.—Mention the chief test for silver, and state how silver salts may be distinguished from those of lead and mercury.—Name the antidote for silver.—Give processes for the qualitative analysis of liquids containing the following substances:—*a.* Antimony and Mercurous salt. *b.* Lead and Calcium. *c.* Silver and Mercurous salt. *d.* Lead and Mercuric salt. *e.* Copper and Arsenium. *f.* Arsenium and Antimony. *g.* Aluminium and Zinc. *h.* Iron and Copper. *i.* Magnesium, Calcium, and Potassium. *j.* Silver, Antimony, Zinc, Barium, and Ammonium.—Enumerate the so-called group-tests for the metals.—Give a general sketch of the method of analysing a solution suspected to contain two or more salts of common metals.—Classify the common metals according to their analytical relations.

METALS OF MINOR PHARMACEUTICAL IMPORTANCE.

Thus far has been considered, somewhat in detail, the chemistry of the common metals, salts of which are frequently used in medicine or in testing medicinal substances. These are:—

Potassium,
Sodium,
Ammonium (?),
Barium,
Calcium,
Magnesium,
Zinc,
Aluminium,
Iron,
Arsenium,
Antimony,
Copper,
Mercury,
Lead,
Silver.

Of the remaining metals, eight are mentioned in the British Pharmacopœia, namely,—

Lithium,
Cerium,
Manganese,
Chromium,
Tin,
Gold,
Platinum,
Bismuth.

Compounds of four more are sufficiently common to occasionally come under notice:—

Strontium, Cobalt, Nickel, Cadmium.

These twelve metals of minor pharmaceutical interest may now be shortly studied, a few only of the reactions of each (just those mentioned in the following pages) being performed. When all have been thus treated, their respective positions in the analytical groups will be indicated and a tabular scheme be given, by which an analysis of a solution containing any metal may be effected. Thus, step by step, we may learn how to analyse almost any substance that may occur, and know to what extent the presence of a rarer will interfere with the ordinary tests for a common element; additional illustrations of the working of chemical laws will be acquired, and the store of chemical and pharmaceutical facts be increased. The opportunity thus afforded for improvement in habits of neatness of manipulation, in precision, and in power of classification furnishes another and no mean reason why such experiments should be prosecuted, the direct value of which may not be considerable to medical and pharmaceutical learners.

LITHIUM.

Symbol, L. Atomic weight, 7.

Lithium is widely distributed in nature, but usually in minute proportions compared with other elements. A trace of it may be found in most soils and waters, a Cornish spring containing even considerable quantities as chloride.

One salt used in medicine is the *Citrate* ($L_3C_6H_5O_7$) (*Lithii Citras*, B.P.), occurring in white deliquescent crystals or powder, prepared by dissolving 50 grains of the carbonate (L_2CO_3) and 90 of citric acid (50 to 95 if both are quite pure) in 1 ounce of water, evaporating to a low bulk, and setting aside in a dry place to crystallize, or at once evaporating to dryness and powdering the residue. The crystals have the formula $L_3C_6H_5O_7$, $4H_2O$; dried at 212° F., $L_3C_6H_5O_7$, H_2O (Umney).

$$\underset{\substack{\text{Carbonate}\\\text{of lithium.}}}{3L_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Citrate of}\\\text{lithium.}}}{2L_3C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

The carbonate (*Lithii Carbonas*, B.P.) is a white granular powder obtained from the minerals which contain lithium—namely, lepidolite (from λεπίς, *lepis*, a scale, and λίθος, *lithos*, a stone; it has a scaly appearance), triphane (from τρεῖς, *treis*, three, and φαίνω, *phainō*, I shine), or spodumene (from σποδόω, *spodŏō*, I reduce to ashes, in allusion to its exfoliation in the blowpipe-flame), and petalite (from πέταλον, *petalon*, a leaf; its character is leafy and laminated). Each contains silicate of aluminium, with fluoride of potassium and lithium in the case of Austrian lepidolite, which is the most abundant source, and silicate of sodium and lithium in the others. The lepidolite is decomposed by sulphuric acid; alumina, etc., precipitated by ammonia; the filtrate evaporated and the residue ignited; the resulting sulphates dissolved in water and the lithium precipitated by a carbonate. The preparation of common alum is sometimes made a part of the factory processes, and other obvious modifications may be introduced. *Liquor Lithiæ Effervescens*, B.P., is a solution of 10 grains of carbonate of lithium in 1 pint of water charged with five times its volume of carbonic acid gas and kept in ordinary aërated-water bottles. "Half a pint, evaporated to dryness, yields 5 grains of a white solid residue, answering to the tests for carbonate of lithium. . . . Ten grains of the latter salt, neutralized with sulphuric acid and afterwards heated to redness, leaves 14·86 grains of dry sulphate of lithium, which, when redissolved in distilled water, yields no precipitate with oxalate of ammonium or solution of lime," indicating absence of salts of calcium and aluminium. Citrate of lithium should yield by incineration 52·8 per cent. of white carbonate of lithium. According to C. N. Draper, carbonate of lithium is soluble in 68 parts of water at 15° C. and 131 at 100° C.

Urate of lithium * is more soluble than urate of sodium; hence lithium preparations are administered to gouty patients in the hope that urate of sodium, with which such systems are loaded, may become urate of lithium and be removed.

In chemical position lithium stands between the alkaline and the alkaline-earth metals, its hydrate, carbonate, and phosphate being slightly soluble in water. The double chloride of platinum and lithium also is soluble in water. The atom of lithium is univalent, L^1.

Analytical Reaction.—Moisten the end of a platinum wire with solution of a minute particle of solid lithium salt, and introduce it into the flame of a Bunsen burner or other almost colourless flame (spirit-lamp or blowpipe-flame); a magnificent crimson tinge is imparted.

The light thus emitted by ignited lithium vapour is of a purer scarlet than that given by strontium, the next element. When the flames are examined by spectral analysis (physically analysed by a prism), the red rays are, in the case of strontium, found to be associated with blue and yellow, neither of which are present in the lithium light, blue lithium rays only appearing at temperatures much higher than those of the air-gas flame, or, indeed, any other ordinary flame.

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* Urates will be considered subsequently in connection with uric acid.

STRONTIUM.

Symbol, Sr. Atomic weight, 87·4.

Source.—Strontium is not widely distributed in nature; but the carbonate ($SrCO_3$), known as *strontianite*, and the sulphate ($SrSO_4$), known as *celestine* (from *cœlum*, the sky, in allusion to its occasional bluish colour), are by no means rare minerals.

Salts of strontium are rarely employed in medicine. They are chiefly used by firework-manufacturers in preparing "red fire." The colour they impart to flame is a crimson—ignited strontium vapour emitting crimson rays, as already explained. Nitrate of strontium ($Sr2NO_3$) is best for pyrotechnic compositions, its oxygen enabling it to burn freely when mixed with charcoal, sulphur, etc. This salt may be obtained by dissolving the carbonate in nitric acid; others similarly or by igniting the cheaper sulphate with coal, whereby sulphide (SrS) is produced, and dissolving this in acid.

The position of strontium among the chemical elements is between barium and calcium; its sulphate is extremely sparingly soluble in water. Its atom, like those of barium and calcium, is bivalent (Sr'').

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To a solution of a strontium salt ($Sr2NO_3$ or $SrCl_2$) add carbonate of ammonium; a white precipitate (carbonate of strontium, $SrCO_3$) falls.

Second Analytical Reaction.—To a solution of a strontium salt add sulphuric acid previously so diluted that it will not precipitate calcium salts, or add an equally dilute solution of any sulphate, *e.g.* that of calcium itself; a white precipitate (sulphate of strontium, $SrSO_4$) falls. The formation of this precipitate is promoted by stirring and by setting the liquid aside for some time. (Barium is precipitated immediately under similar circumstances.)

Third Analytical Reaction.—To a dilute solution of a strontium salt add yellow chromate (K_2CrO_4 or KNH_4CrO_4); no precipitate falls.

Barium may be separated from strontium by chromate of potassium, that reagent at once precipitating barium from aqueous or acetic solutions. The value of the reaction is enhanced if acetic acid or acetate of ammonium be present, chromate of strontium being far more soluble in such fluids than in water (Ransom). It is also more soluble in cold than in hot fluids.

Fourth Analytical Reaction.—Insert a fragment of a strontium salt in the blowpipe-flame, or other equally colourless flame, or hold the end of a platinum wire dipped into a strontium solution in the flame; a crimson colour is imparted.

Other Analytical Reactions. — Alkali-metal phosphates, arseniates and oxalates give white insoluble precipitates with strontium as with barium and calcium.

CERIUM. Ce. At. wt., 141.—This element occurs in the mineral cerite (a silicate of iron, calcium, and the three rare metals, cerium, lanthanium, and didymium); also occasionally as impure fluoride, carbonate, and phosphate. The oxalate of cerium, a white granular powder, is the only official salt; it may be obtained from cerite by boiling the powdered mineral in strong hydrochloric acid for several hours, evaporating, diluting, and filtering to separate silica; adding ammonia to precipitate hydrates of all the metals except calcium; filtering off, washing, redissolving in hydrochloric acid, and adding oxalic acid to precipitate oxalate of cerium. The preparation will still contain oxalates of lanthanium and didymium; it is therefore strongly calcined, the resulting oxides of lanthanium and didymium dissolved out to some extent by boiling with a concentrated solution of chloride of ammonium, the residual oxide of cerium dissolvod in boiling hydrochloric acid, and oxalate of ammonium addod to precipitate oxalate of cerium ($Ce'''_2 3C_2O_4, 9H_2O$). According to Hartley, the precipitated hydrates should be treated with chlorine, by which ceric hydrate is loft insoluble and the other hydratcs convcrted into soluble hypochloritos.

Oxalate of cerium (*Cerii Oxalas*, B.P.) is decomposed at a dull-red heat, 48 per cent. of a yellow or, more generally, salmon-coloured mixture of oxides remaining. Usually the didymium present gives the ignited residue a reddish or reddish-brown colour. The oxides are soluble in boiling hydrochloric acid (without effervescence, indicating, indirectly, absence of earthy and other carbonates or oxalates); and the solution gives, with excess of a saturated solution of sulphate of potassium, a crystalline precipitate of double sulphate of cerium and potassium. Alumina mixed with oxalate of cerium may be detected by boiling with solution of potash, filtering, and adding excess of solution of chloride of ammonium, when a white flocculent precipitate (hydrate of aluminium) will be obtained. The oxalic radical is recognised by neutralizing the potash solution by acetic acid and adding chloride of calcium; a white precipitate (oxalate of calcium) falls: this precipitate, though insoluble in acetic, should be wholly dissolved by hydrochloric acid. Acid or neutral cerium solutions give with acetate of sodium and peroxide of hydrogen a brownish-red colour (Hartley).

According to Greenish, most samples of the oxalate contain as impurities traces of lead, iron, and magnesium.

MANGANESE.

Symbol, Mn. Atomic weight, 55.

Source.—Manganese is a constituent of many minerals, and, as black oxide, (MnO_2) (*Manganesii Oxidum Nigrum*, B.P.), or *pyrolusite* (from πῦρ, *pur*, fire, and λύσις, *lusis*, a loosing or resolving, in allusion to the readiness with which it is split up by heat into a lower oxide and oxygen), is met with in abundance in the south-west of England, Aberdeenshire, and most countries of Europe. It occurs as a steel-grey mass of prismatic crystals, or in black shapeless lumps.

The chemical position of manganese is close to iron and three other metals still to be considered—cobalt, nickel, and chromium. Its atom apparently has sexivalent affinities, as seen in manganate of potassium (K_2MnO_4); but commonly it is quadrivalent (Mn'''') or bivalent (Mn'').

Uses.—Metallic manganese, which may be isolated by aid of sodium, is used in alloy with iron in the manufacture of some varieties of steel. The black oxide is an important agent in the production of chlorine, and in the preparation of green and purple disinfecting manganates, purple glass, and black glaze for earthenware.

REACTIONS HAVING BOTH SYNTHETICAL AND ANALYTICAL INTEREST.

First Reaction.—Boil a little black oxide of manganese with hydrochloric acid in a fume-chamber until chlorine ceases to be evolved; filter; the filtrate is a solution of manganous chloride ($MnCl_2$). $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$.

This is the reaction commonly applied in the preparation of chlorine gas. It is also a ready method of preparing a manganous salt for analytical experiments. Coupled with the application of reagents to the filtrate, the reaction is that by which a black powder or mineral would be recognised as black oxide of manganese. Black oxide of manganese dissolves in *cold* hydrochloric acid, forming a dark brown solution of a higher chloride or chlorides, $MnCl_3$, Mn_2Cl_7, or, possibly, $MnCl_4$.

Second Reaction.—Heat a manganese compound with a grain or two of carbonate and hydrate of potassium and a fragment of nitrate or chlorate of potassium on platinum foil in the blowpipe-flame; a green mass containing *manganate of potassium* (K_2MnO_4) results. Boil the foil in water; the green manganate dissolves, the fluid soon changing to solution of the purple *permanganate of potassium* ($K_2Mn_2O_8$).

Carefully performed, this is a delicate test for manganese. The reaction is similar to that by which permanganate of potassium (*Potassii Permanganas*, B.P.) is directed to be prepared for use in volumetric analysis. *Liquor Potassii Permanganatis*, B.P., is a solution of 88 grains of permanganate of potassium in 1 pint of distilled water. Equations showing the exact action which occurs in making the salt according to the process of the British Pharmacopœia have already been given in connection with the compounds of potassium (*vide* p. 81). The proportions of ingredients and details of the operation are as follows:—

Reduce 3½ parts (for experiment each "part" may be ⅛ ounce) of chlorate of potassium to fine powder, and mix it with 4 of black oxide of manganese; put the mixture into a porcelain basin, and add to it 5 parts of solid caustic potash, previously dissolved in 4 parts of water. Evaporate to dryness, stirring diligently to prevent spurting. Pulverize the mass, put it into a covered Hessian or Cornish crucible, and expose it to a dull red heat (not higher) for an hour (20 or 30 minutes for quantities of 1 or 2 ounces), or till it has assumed the condition of a semi-fused mass. Allow to cool, pulverize, and boil with about 30 parts of water. Let the insoluble matter subside, decant the fluid, boil again with about 10 parts of water, again decant, neutralize the united liquors accurately with diluted sulphuric acid (or better, carbonic acid gas), and evaporate till a pellicle forms. Set aside to cool and crystallize. Drain the crystalline mass, boil it in 6 parts of water, and strain through a funnel the throat of which is lightly obstructed by a little asbestos or gun-cotton. Let the fluid cool and crystallize, drain the dark-purple, slender, prismatic crystals, and dry them by placing under a bell-jar over a vessel containing sulphuric acid.

Instead of converting the manganate by ebullition, and neutralizing the free alkali by acid, by which one-third of the manganese is lost, chlorine may be passed through the cold solution until the green colour is entirely changed to purple. $2K_2MnO_4 + Cl_2 = K_2Mn_2O_8 + 2KCl$.

Solutions of the manganates of potassium and sodium are in common use as green and purple disinfecting fluids. They act by oxidizing organic matter, the manganic or permanganic radical being reduced to black manganic oxide, or even a lower oxide. The reason for using asbestos instead of paper in filtering the solutions will now be understood.

The changes in colour which the green mass of the above process undergoes when dropped into warm water produced for it the old name of *mineral chameleon*.

Third Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of a manganese compound, or touch it with a drop of solution. Again fuse the borax; a bead of a violet or amethystine tint is produced.

This is a good analytical reaction. It has also synthetical interest, illustrating the use of black oxide of manganese in producing common purple-tinted glass.

Expose the bead to the reducing part of the flame (p. 150), the part nearer to the blowpipe, where there are highly heated hydrocarbon gases greedy of oxygen; the colour disappears.

This is owing to the reduction of the manganic compound to a manganous condition, in which it no longer possesses peculiar colouring-power. This action also illustrates the use of black oxide of manganese in glass-manufacture. Glass, when first made, is usually of a green tint, owing to the presence of ferrous impurities; the addition of manganic oxide to the materials converts the ferrous into ferric compounds, which have comparatively little colorific power, it itself being thereby reduced to manganous oxide, which also gives but little colour. If excess of manganic oxide be added, a purple tint is produced.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

Fourth Reaction.—Through a solution of a manganous salt acidified by hydrochloric acid pass sulphuretted hydrogen; no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes the precipitation of a yellowish-pink or flesh-tinted precipitate (manganous sulphide, MnS, in a hydrous state).

This reaction is characteristic, sulphide of manganese being the only flesh-coloured sulphide known. The salt used may be the manganous chloride obtained in the first reaction; but such crude solutions usually give a black precipitate with sulphydrate of ammonium, owing to the presence of iron. The latter element may be precipitated, however, on adding excess of ammonia (and rapidly filtering, or oxygen will be absorbed and most of the manganese also be precipitated) or on boiling the manganous solution with a very little carbonate of sodium, which attacks the ferric salt in preference to the manganous. *Pure* manganous chloride may be similarly obtained on boiling the impure solution with manganous carbonate; the latter decomposes the ferric chloride, with production of ferric hydrate and more manganous chloride and evolution of carbonic acid gas.

To the recently precipitated manganous sulphide add acetic acid; it is dissolved.

This solubility enables manganese to be separated from nickel, cobalt, and zinc, whose sulphides are insoluble in weak acetic acid. To express the fact in another way—manganese is not precipitated by sulphuretted hydrogen from a solution containing free acetic acid.

Fifth Reaction.—To solution of a manganous salt add ammonia; a white precipitate (manganous hydrate, Mn2HO) falls. Add excess of ammonia; some of the precipitate is dissolved, and may be detected in the quickly filtered solution by sulphydrate of ammonium. But both precipitate and solution rapidly absorb oxygen, the manganese passing into a more highly oxidized condition, in which it is insoluble in ammonia. The fixed alkalies give a similar precipitate *insoluble* in excess. The precipitate rapidly absorbs oxygen, becomes brown, and gradually passes into a higher oxide.

Sixth Reaction.—To a solution of a manganous salt add diluted nitric acid, and either red lead or the puce-coloured oxide or peroxide of lead, and then boil; a red tint, said to be due to permanganic acid, is imparted to the liquid. If chlorides are present, the manganese, etc., should be separated by potash or soda, the precipitate be well washed, dissolved in nitric acid, and then the oxide be added. (Crum.)

Many other reactions occur between manganese salts and various reagents, but are of no particular synthetical or analytical interest.

COBALT AND NICKEL.

Krüss and Schmidt state that these very closely allied metals, as hitherto known, are not true elements, but contain a third element, the oxide of which resembles, yet distinctly differs from, alumina and oxide of zinc.

COBALT.

Symbol, Co. Atomic weight, 58·6.

Source.—Cobalt occurs sparingly in Nature as the arsenide ($CoAs_2$), or *tin-white cobalt*, and occasionally as a double arsenide and sulphide ($CoAs_2$, CoS_2), or *cobalt-glance* (from *glanz*, brightness, in allusion to its lustre).

Uses.—Its chief use is for colouring glass blue. Cobalt is also the colouring constituent of *smalt* (from *smelt*, a corruption of *melt*), a finely ground sort of glass used as a blue pigment by paper-stainers and others, and employed also by laundresses to neutralize the yellow tint of washed linen.

The salts of cobalt may be obtained from the oxide (CoO), and the oxide from *zaffre*, a mixture of sand and roasted ore.

Quantivalence.—The atom of cobalt often exhibits quadrivalent affinities, but still more often exerts only bivalent powers (Co''). Cobalt has analytical relations with zinc, nickel, and manganese.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a salt of cobalt—the chloride ($CoCl_2$) or nitrate ($Co2NO_3$) for example; no decomposition occurs. Add ammonia; the sulphydrate of ammonium thus formed causes a black precipitate (sulphide of cobalt, CoS). (The moist precipitate slowly absorbs oxygen from the air, yielding some sulphate of cobalt, $CoSO_4$.)

Second Analytical Reaction.—Add ammonia gradually to a cobalt solution; a blue precipitate (impure hydrate of cobalt, Co2HO) falls. Add excess of ammonia; the precipitate is dissolved, yielding a liquid somewhat more reddish-brown than the original solution. A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Make a borax bead by heating a fragment of the salt on the looped end of a platinum wire in the blowpipe-flame until a clear transparent globule is obtained. Place on the bead a minute portion of any cobalt compound, or touch it with a drop of solution. Again fuse the borax; a blue bead results.

This is a delicate test for cobalt. From what has been said previously, it will be seen that this experiment has also considerable synthetical interest.

Fourth Analytical Reaction.—To a solution of a salt of cobalt add a few drops of hydrochloric acid, then excess of solution of cyanide of potassium, and boil for ten minutes; oxygen is absorbed, and cobalticyanide of potassium ($K_6Co_2Cy_{12}$) formed. Add hydrochloric acid, and boil the mixture (in a fume-cupboard, to avoid inhalation of any hydrocyanic acid); the excess of cyanide of potassium is thus decomposed, the cobalticyanide unaffected. Now add *excess* of solution of potash; the cobalticyanide of potassium is probably decomposed, but the cobalt remains dissolved in the alkaline liquid. Nickel under similar circumstances is precipitated, the reaction thus affording means of separating these closely allied metals from each other.

Other reactions between a cobalt solution and different reagents may be performed, and various precipitates obtained; but these have no special analytical interest.

Invisible Ink.—Many salts of cobalt containing water of crystallization are light red, the anhydrous more or less blue. Prove this by writing some words on paper with a solution of chloride of cobalt sufficiently dilute for the characters to be invisible when dry: hold the sheet before a fire or over a flame; the letters at once become visible, distinct, and of a blue colour. Breathe on the words, or set the sheet aside for a while; the characters are once more invisible, owing to absorption of moisture. Hence solution of chloride of cobalt forms one of the so-called *sympathetic inks.*

NICKEL.

Symbol, Ni. Atomic weight, 58·6.

The ores of nickel and cobalt are, commonly, associated in nature. Indeed it is from *speiss*, an arsenio-sulphide of nickel obtained in the manufacture of a pigment of cobalt, smalt, already mentioned, that much of the nickel met with in commerce has hitherto been obtained. *Garnierite*, silicate of magnesium and of nickel, containing no cobalt, is also a valuable source of cobalt. Nickel is used in the preparation of the white alloy known as German or nickel silver, and for plating iron.

Quantivalence.—Nickel exerts bivalent activity (Ni'') in its ordinary compounds. Its salts and their solutions are usually green. They are chiefly made, directly or indirectly, from the metal itself.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—Pass sulphuretted hydrogen through an acidified solution of a salt of nickel—chloride ($NiCl_2$), nitrate ($Ni2NO_3$), or sulphate ($NiSO_4$); no decomposition occurs. Add ammonia; the sulphydrate of ammonium formed causes a black precipitate (sulphide of nickel, NiS).

Note.—When sulphide of nickel is precipitated by the direct addition of the common yellow solution of sulphydrate of ammonium, which always contains free sulphur, there is much difficulty in filtering the mixture, owing to the slight solubility of sulphide of nickel in the reagent and the formation of some sulphate of nickel ($NiSO_4$), oxygen being absorbed from the air by the sulphide. This may be avoided by warming the mixture and using freshly made sulphydrate of ammonium, in which the sulphide of nickel is insoluble; or, when practicable, the salt of nickel may be precipitated from an ammoniacal solution by sulphuretted hydrogen.

Second Analytical Reaction.—Add ammonia drop by drop to a nickel solution; a pale-green precipitate (hydrate of nickel, $Ni2HO$) falls—especially on boiling the mixture. Add excess of ammonia; the precipitate dissolves, yielding a bluish rather than the original green-coloured solution. A similar precipitate is given by the fixed alkalies, *insoluble* in excess.

Third Analytical Reaction.—Nickel salts colour a borax bead, when hot, a reddish-yellow tint; the reaction is not very serviceable analytically.

Fourth Analytical Reaction.—To a solution of a salt of nickel add solution of cyanide of potassium; cyanide of nickel ($NiCy_2$) is precipitated. Add excess of solution of cyanide of potassium; the precipitate is dissolved with formation of double cyanide of nickel and potassium ($NiCy_2$, $2KCy$). Next add hydrochloric acid, and boil the mixture (in a fume-cupboard, adding a little hydrochloric acid from time to time until all smell of hydrocyanic acid has disappeared). Lastly, add *excess* of solution of potash; pale-green hydrate of nickel is precipitated.

Qualitative separation of Cobalt and Nickel.

(*This process requires much practice for its successful performance, and need not be attempted by pupils whose studies are restricted to medicine or pharmacy.*)

The foregoing reaction serves for the separation of nickel from cobalt. On adding excess of cyanide of potassium to a very slightly acidified solution containing the two metals, and well boiling, a solution of cobalticyanide of potassium and double cyanide of nickel and potassium results. On boiling with excess of hydrochloric acid, the nickel salt is converted into chloride, and this with the cobalticyanide of potassium, gives a milky-looking precipitate of cobalticyanide of nickel ($Ni_3Co_2Cy_{12}$), insoluble in the acid. On then adding excess of potash, the cobalticyanide of nickel is decomposed, nickel hydrate remaining as a green flocculent precipitate, and cobalticyanide of potassium going into solution. After filtering off the nickel, cobalt is detected in the filtrate by evaporating to dryness and testing the residue with borax in the blowpipe-flame.

Other reactions between a nickel solution and various reagents give, in many cases, insoluble precipitates which, from their green colour, are occasionally useful in distinguishing nickel from allied elements.

CHROMIUM.

Symbol, Cr. Atomic weight, 52·5.

Source.—The chief ore of chromium is chrome ironstone (a compound of the metallic oxides FeO, Cr_2O_3), occurring chiefly in the United States and Sweden. In constitution it seems to resemble magnetic iron ore (FeO, Fe_2O_3). The metal may be isolated by aid of sodium.

Preparation of Red Chromate of Potassium.—On roasting the powdered ore with carbonate of potassium and nitre, yellow chromate of potassium (K_2CrO_4) is obtained; the mass, treated with acid, yields red or bichromate (K_2CrO_4, CrO_3) (*Potassii Bichromas*, B.P.), the old *bichromate of potash*; from this other chromates are prepared, and, by reduction, as presently explained, the salts of chromium itself. The yellow and orange chromates of lead are used as pigments.

Notes.—Red chromate of potassium is a somewhat abnormal salt, containing, possibly, neutral chromate associated with chromic anhydride, and hence termed *anhydrochromate of potassium* (K_2CrO_4, CrO_3) or *pyrochromate of potassium* ($K_2Cr_2O_7$). The value of chromates as chemical reagents is alluded to in connection with chromate of barium (pp. 110 and 127). Heated strongly in a crucible, red chromate of potassium splits up into yellow chromate, glistening oxide of chromium, and oxygen. Red chromate of ammonium by heat yields several times its volume of bluish-green oxide of chromium, water, and nitrogen. $(NH_4)_2CrO_4, CrO_3 = Cr_2O_3 + 4H_2O + N_2$.

Quantivalence.—Chromium stands in close chemical relation to iron, aluminium, and manganese. Its atom is sexivalent if the formula of the fluoride (CrF_6) be correct. Like iron and aluminium, it is trivalent, as seen in chromic chloride (Cr_2Cl_6), but sometimes exerts only bivalent activity, as in chromous chloride ($CrCl_2$).

Passage of chromium from the acidulous to the basylous side of salts.—Through an acidified solution of red chromate of potassium pass sulphuretted hydrogen; sulphur is deposited, and a green salt of chromium remains in solution—chloride (Cr_2Cl_6) if hydrochloric acid be used, and sulphate (Cr_23SO_4) if sulphuric be the acid employed. Boil the liquid to expel excess of sulphuretted hydrogen, filter, and reserve the solution for subsequent experiments. (For an equation explanatory of this reaction, *see* p. 275.) Alcohol, sugar, or almost any substance which is tolerably liable to oxidation will answer as well as sulphuretted hydrogen.

Sulphate of chromium (Cr_23SO_4), like sulphate of aluminium (Al_23SO_4), unites with alkali-metal sulphates to form *alums*, which resemble common alum both in crystalline form and in structure: they are of a purple colour.

REACTIONS.

Chromium as *chromic acid* or other *chromate*. This is the state in which chromium will usually be met with, the most common salt being the red chromate or bichromate of potassium. Mix four volumes of a cold saturated aqueous solution of red chromate of potassium with five of oil of vitriol; on cooling, *chromic anhydride*, or *anhydrous chromic acid* (CrO_3) (*Acidum Chromicum*, B.P.) separates in crimson needles. After well draining, the crystals may be freed from adhering sulphuric acid by washing once or twice with nitric acid: the latter may be removed by passing dried and slightly warmed air through a tube containing the crystals. It may also be freed from sulphuric acid by one or two recrystallizations. In contact with moisture, chromic anhydride takes up water and forms solution of true chromic acid (H_2CrO_4), 1 part of the anhydride and 3 of water forming the *Liquor Acidi Chromici*, B.P. Chromic anhydride is a powerfully corrosive oxidizing agent; it melts between 356° and 374° F., and at a higher temperature decomposes, yielding oxide of chromium and oxygen; it oxidizes organic matter with great violence.

The oxygen in chromic acid and other chromates, and in manganates, permanganates, black oxide of manganese, and puce-coloured oxide of lead, is in a physically different state to that in peroxide of hydrogen, peroxide of barium, and similar compounds. On bringing chromic acid, or the above acidified solution of red chromate of potassium, into contact with solution of peroxide of hydrogen, a strong effervescence of oxygen ensues. According to Schönbein and Brodie, the oxygen in chromic acid is in the negative or ozonic state, while that of peroxide of hydrogen is in the positive or so-called antozonic condition. Both are equally active, but neutralize each other, forming neutral or ordinary oxygen.

In the analytical examination of solutions containing chromates, the chromium will always come out in the state of green chromic hydrate along with ferric hydrate and alumina, the prior treatment by sulphuretted hydrogen reducing the chromium in the molecule to the lower state, thus:—

$$K_2CrO_4, CrO_3 + 8HCl + 3H_2S = Cr_2Cl_6 + 2KCl + 7H_2O + S_3.$$

Chromium having been found in a solution, its condition as chromate may be ascertained by applying to the original solution salts of barium, mercury, lead, and silver. (*See* the various paragraphs relating to those metals.)

$Ba2NO_3$	gives	yellow	$BaCrO_4$	with chromates.
$HgNO_3$	,,	red	Hg_2CrO_4	,,
$AgNO_3$	,,	red	Ag_2CrO_4	,,
$AgNO_3$	,,	red	Ag_2CrO_4, CrO_3	with bichromates.
$Pb2C_2H_3O_2$	,,	yellow	$PbCrO_4$,	with both.

Nitrate of barium does not completely precipitate bichromates, bichromate of barium being soluble in water; the chromate of barium is insoluble in water or acetic acid, but soluble in hydrochloric or nitric acid. Mercurous nitrate does not wholly precipitate bichromates: mercuric nitrate or chloride only partially precipitates chromates, and does not precipitate bichromates. The mercurous chromate is insoluble, or nearly so, in diluted nitric acid. The silver chromates are soluble in acids and alkalies. Acetate of lead precipitates chromates and bichromates, acetic acid being set free in the latter case.

A delicate reaction for dry chromates will be found in the formation of *chlorochromic anhydride* (CrO_2Cl_2). A small portion of the chromate is placed in a test-tube with a fragment of dry chloride of sodium and a drop or two of sulphuric acid, and the mixture heated; red irritating fumes of chlorochromic anhydride are evolved and condense in dark red drops on the side of the tube.

Larger quantities are obtained by the same reaction, the operation being conducted in a retort, with thoroughly dry materials, for the compound is decomposed by water. It may be regarded as chromic anhydride in every molecule of which an atom of oxygen is displaced by an equivalent quantity (two atoms) of chlorine. It is not used in medicine, but is of interest to the chemical student as being an illustration of a class of similar bodies—*chloro-acidulous* or *chloro-anhydro compounds.* The reaction is also occasionally serviceable for the detection of chlorides.

ANALYTICAL REACTIONS OF CHROMIUM SALTS (TESTS).

First Analytical Reaction.—To solution of a salt of chromium (chloride, sulphate, or chrome alum) add sulphydrate of ammonium; a bulky green precipitate (chromic hydrate, Cr_26HO), containing a large quantity of water (7 molecules, $7H_2O$), is precipitated.

$$Cr_2Cl_6 + 6NH_4HS + 6H_2O = Cr_26HO + 6NH_4Cl + 6H_2S.$$

Second Analytical Reaction.—To solution of a chromium salt add ammonia; green chromic hydrate is precipitated, insoluble in excess.

Third Analytical Reaction.—To solution of a chromium salt add solution of potash or soda drop by drop; green chromic hydrate is precipitated. Add excess of the fixed alkali; the precipitate is dissolved. Well boil the solution; the green chromic hydrate is reprecipitated.

Iron, Chromium, and Aluminium Salts, chemically so alike, may be separated by this reaction. Ferric hydrate is insoluble in solutions of the fixed alkalies, cold or hot; chromium hydrate soluble in cold but not in hot; hydrate of aluminium in both. To a solution containing all three metals, therefore, add potash or soda, stir, and filter; the iron is thrown out; boil the filtrate, and filter; the chromium is thrown out: neutralize the latter filtrate by acid, and then add ammonia; the aluminium is thrown out. Note, however, that ferric hydrate will prevent hydrate of chromium being dissolved by potash or soda if the ferric hydrate is in considerable excess. Before concluding that chromium is entirely absent, the fourth reaction should be performed. The hydrates of iron, chromium, and aluminium are insoluble in ammonia, and may therefore easily be separated from the hydrates of the somewhat analogous metals, zinc, cobalt, nickel, and manganese.

Fourth Analytical Reaction.—Add a salt of chromium (either of the above precipitates of chromic hydrate or the dry residue of the evaporation of a few drops of a solution of a chromium salt) to a few grains of nitre and carbonate of sodium on platinum foil, and fuse the mixture in the blowpipe-flame; a yellow mass (chromate of potassium and sodium, $KNaCrO_4$) is formed. Dissolve the mass in water, add acetic acid to decompose excess of carbonate, and apply the reagents for chromates. This is a delicate and useful reaction if carefully performed.

TIN.

Symbol, Sn. Atomic weight, 118.

Source.—The chief ore of tin is stannic oxide (SnO_2), occurring in veins under the name of *tinstone*, or in alluvial deposits as *stream-tin*. The oldest mines are those of Cornwall. Much tin is now imported from Australia.

Preparation.—The metal is obtained by reducing the roasted and washed ore by charcoal or anthracite[*] coal at a high temperature, and is purified by slowly heating, when the pure tin, fusing first, is run off, a somewhat less fusible alloy of tin, with small quantities of arsenium, copper, iron, or lead remaining. The latter is known as *block tin*; the former heated till brittle and then hammered or let fall from a height splits into prismatic fragments resembling starch or columnar basalt, and is named *dropped* or *grain tin*. Good tin emits a crackling noise in bending, termed the cry of tin, caused by the friction of its crystalline particles on each other.

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[*] *Anthracite* (from ἄνθραξ, *anthrax*, a burning coal), or *stone coal*, differs from the ordinary *bituminous* or *caking coal* in containing less volatile matter, and, therefore, in burning without flame. It gives a higher temperature, and from its non-caking properties is, in furnace operations, more manageable than bituminous coal.

Uses.—Tin is an important constituent of such alloys as pewter, Britannia metal, solder, speculum-metal, bell-metal, gun-metal, and bronze. It is very ductile, and may be rolled into plates, or leaves, known as *tin foil*, varying from $\frac{1}{250}$ to $\frac{1}{1000}$ of an inch in thickness. Common tin foil, however, usually contains a large proportion of lead. The reflecting surface of *looking-glasses* was, formerly, always an amalgam of tin and mercury, produced by carefully sliding a plate of glass over a sheet of tin foil on which mercury had been rubbed and then excess of mercury been poured—but pure silver, deposited from a solution, is now largely employed. *Pins* are made of brass wire on which tin is deposited. *Tin plate*, of which common utensils are made, is iron alloyed with tin by dipping the acid-cleansed sheet into vessels of melted tin covered with melted chloride of zinc in the one case and oil in the other; fluids which, by dissolving any trace of oxide, or by preventing oxidation, enable the tin more completely to alloy with the iron. *Tin tacks* are in reality tinned iron tacks, a tin nail would be too soft to drive into wood. Tin may be granulated by melting and triturating briskly in a hot mortar, by shaking melted tin in a box on the inner sides of which chalk has been rubbed, or, in thin little bells or corrugated fragments (Granulated Tin, B.P.), by melting in a ladle and, immediately it is fluid, pouring from the height of a few feet into water. Powdered tin has been used medicinally as a mechanical irritant to promote expulsion of worms. The hairs of the pod of *Kiwach* (Hindustani) or *Cowhage* (*Mucuna pruriens*) (P.I.) is almost the only other medicine (excluding diluents and dentifrices) which acts in such a directly mechanical manner.

The chemical position of tin among the metals is close to that of arsenium and antimony. Its atom is quadrivalent, Sn'''', and bivalent, Sn''. The two classes of salts are termed stannic and stannous respectively.

REACTIONS HAVING SYNTHETICAL INTEREST.

Chloride of Tin. Stannous Chloride.

First Synthetical Reaction.—Warm a fragment of tin with hydrochloric acid; hydrogen escapes and solution of stannous chloride ($SnCl_2$, perhaps Sn_2Cl_4) is formed. It may be retained for future experiments.

One ounce of tin dissolved in three fluid ounces of hydrochloric acid and one of water, and the resulting solution diluted to five fluid ounces, constitutes the "Solution of Stannous Chloride," B.P.

Solid stannous chloride.—By evaporation of the above solution, stannous chloride is obtainable in crystals ($SnCl_2$, $2H_2O$). It is a powerful reducing agent, even a dilute solution precipitating gold, silver, and mercury from their solutions, converting ferric and cupric into ferrous and cuprous salts, and partially deoxidizing arsenic, manganic, and chromic acids. It absorbs oxygen from the air, and is decomposed when added to a large quantity of water unless some acid be present. It is used as a mordant in dyeing and calico-printing.

Perchloride of Tin. Stannic Chloride.

Second Synthetical Reaction.—Through a portion of the solution of the stannous chloride of the previous reaction pass chlorine gas; solution of stannic chloride ($SnCl_4$) is formed. Or add hydrochloric acid to the stannous solution, boil, and, in a fume-chamber, slowly drop in nitric acid until no more fumes are evolved; again stannic chloride results. Reserve the solutions for subsequent experiments.

Stannic Oxide or Anhydride and Stannates.

Third Synthetical Reaction.—Boil a fragment of tin with nitric acid, evaporate to dryness, and strongly calcine the residue; light buff-tinted stannic anhydride (SnO_2) is produced. Heat the stannic anhydride with excess of solid caustic potash or soda; stannate of the alkali metal (K_2SnO_3

or Na_2SnO_3) results. Dissolve the stannate in water, and add hydrochloric acid; white, gelatinous *stannic acid* (H_2SnO_3) is precipitated. Stannic acid is also obtained on adding an alkali to solution of stannic chloride; it is soluble in excess of acid or alkali.

The product of the action of nitric acid on tin is also an acid, but, from its insolubility in hydrochloric and other acids, is different from ordinary stannic acid. It is termed *meta-stannic acid* (from μετὰ, *meta*, beyond), and its molecule probably has a composition expressed by the formula $H_{10}Sn_5O_{15}$ (*vide* Index, "Isomerism"). It is also produced on gently heating stannic acid:—

$$\underset{\text{Stannic acid.}}{5H_2SnO_3} = \underset{\text{Metastannic acid.}}{H_{10}Sn_5O_{15}}$$

Metastannates have the general formula $M'_2H_8Sn_5O_{15}$.

Both acids yield buff-coloured stannic oxide or anhydride (SnO_2) when strongly heated. The latter is employed in polishing plate under the name of *putty powder*. *Stannate of sodium* ($Na_2SnO_3,4H_2O$) is used as a mordant by dyers and calico-printers under the name of *tin prepare-liquor*.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

Stannous or stannic salts.—Heat any solid compound of tin with a mixture of cyanide of potassium and carbonate of sodium on charcoal by the inner flame of the blowpipe. Hard globules of tin separate, having, when cut by a knife, characteristic brightness and whiteness.

Stannous Salts.

First Analytical Reaction.—Through a diluted solution of a stannous salt (stannous chloride, for example) pass sulphuretted hydrogen gas; a brown precipitate (stannous sulphide, SnS) results. Pour off the supernatant liquid, add ammonia to the moist precipitate (to neutralize acid), and, lastly, yellow sulphydrate of ammonium solution; the precipitate is dissolved.

Aqueous solution of sulphydrate of ammonium becomes yellow when a day or two old, and then contains excess of sulphur, some of that element having become displaced by oxygen absorbed from the air; hence in the above reaction the stannous sulphide (SnS), in dissolving, becomes stannic sulphide (SnS_2); for the latter is precipitated on decomposing the alkaline liquid by an acid.

Second Analytical Reaction.—To solution of a stannous salt add solution of potash or soda: a white precipitate falls (stannous hydrate, $Sn2HO$). Add excess of the alkali; the precipitate dissolves. Boil the solution; some of the tin is reprecipitated (as blackish stannous oxide, SnO). Ammonia gives a similar white precipitate, insoluble in excess. The alkaline carbonates do the same, carbonic acid gas escaping.

Stannic Salts.

Third Analytical Reaction.—Through solution of a stannic salt (stannic chloride, for example) pass sulphuretted hydrogen gas; a yellow precipitate results (stannic sulphide, SnS_2). Pour off the supernatant liquid, and to the moist precipitate add ammonia (to neutralize acid), and then sulphydrate of ammonium; the precipitate dissolves.

Note.—In this reaction the presence of much hydrochloric acid must be avoided; the formation of the precipitate is also facilitated if the solution be warmed. Stannic sulphide, like the sulphides of arsenium and antimony, dissolves in a solution of alkaline sulphide or sulphydrate, with formation of definite crystallizable *sulphostannates* (M'_2SnS_3).

Anhydrous stannic sulphide, prepared by sublimation, has a yellow or orange lustrous appearance, and is known as *mosaic gold.* It was formerly used by decorators as *bronzing-powder*, but the latter is now commonly powdered *bronze-leaf.*

Fourth Analytical Reaction.—To solution of a stannic salt add potash or soda; a white precipitate appears (stannic acid, H_2SnO_3). Add excess of the alkali; the precipitate dissolves. Boil the mixture; no reprecipitation occurs—a fact enabling stannic to be distinguished from stannous salts.

Ammonia gives a similar precipitate slowly soluble in excess. The fixed alkali-metal carbonates do the same, carbonic acid gas escaping; after a time the stannic salt is again deposited, probably as stannate of the alkali-metal. Carbonate of ammonium and all the bicarbonates give a precipitate of stannic acid insoluble in excess.

Antidotes.—In cases of poisoning by tin salts (dyers' tin-liquor, *e.g.*), solution of carbonate of ammonium should be given; and white of egg is also said to form an insoluble precipitate. Vomiting should be induced, and the stomach-pump, or stomach-siphon, applied.

GOLD.

Symbol, Au. Atomic weight, 196·85.

Source.—Gold occurs in the free state in nature, occasionally in nodules or *nuggets*, but commonly in a finer state of division termed *gold dust*.

Preparation.—Gold is separated from sand, crushed quartz, or other earthy matter with which it may be associated, by agitation with water, when the gold, from its relatively greater specific gravity, falls to the bottom of the vessel first, the lighter mineral matter running off with the water. From this rich sand the gold is dissolved out by mercury, the amalgam filtered and afterwards distilled, when the mercury volatilizes and gold remains. The amalgamation may be facilitated by the use of sodium, as already described in treating of silver. From even the poorest ores gold may be dissolved by solution of cyanide of potassium. (See Faraday on gold leaf, 1857.) $4KCy + Au_2 + O + H_2O = 2AuKCy_2 + 2KOH$. Elkington deposited the metal by aid of a battery, of which the *anode* or positive pole was a plate of gold, in 1840, deposition taking place at the *cathode* or negative pole (ανα, *ana*, upward or onward; κατα, *kata*, downward; ὁδος, *odos*, way). The gold solution was made, as now, from the chloride of gold and cyanide of potassium, chloride and aurocyanide of potassium ($AuKCy_2$) being formed: but Elkington, in 1857, made it direct from a gold anode with a small cathode in solution of cyanide of potassium.

Pure gold is too soft for general use as a circulating medium. *Gold coin* is an alloy of copper and gold, that of Great Britain containing 1 of the former to 11 of the latter, or $8\frac{1}{3}$ per cent. of copper, that of France, Germany, and the United States about ten per cent. *Jewellers' gold* varies in quality, every 24 parts containing 18, 15, 12, or 9 parts of gold, the alloys being technically termed 18, 15, 12, or 9 *carat fine*, the reckoning being in the old "parts per 24," instead of the more usual parts per cent. Articles made of the better qualities are usually stamped by authority. Trinkets of inferior intrinsic worth are commonly thinly coated with pure gold by electro-deposition or otherwise. The so-called *mystery gold* is an alloy of about 1 part platinum and 2 parts copper with a little silver. It resists the action of strong nitric acid. The action of aqua regia and then ammonia reveals its cupric character. *Gold leaf* is nearly pure gold passed between rollers till it is about $\frac{1}{800}$ of an inch in thickness and then hammered between sheets of animal membrane, termed gold-beaters' skin and calf-skin vellum, till it is $\frac{1}{160000}$ or $\frac{1}{200000}$ of an inch in thickness. It may even be hammered till 280,000 leaves would be required to form a pile an inch thick.

Gold Coinage.—The weight of gold is expressed in this country in ounces troy and decimal parts of an ounce; and the metal is always taken to be of standard fineness (11 gold and 1 alloy), unless otherwise described. The degree of "fineness" of gold, as ascertained by assay, is expressed decimally, fine pure gold ("gold free from metallic impurities," B.P.) being taken as unity, or 1·000. Thus gold of British standard is said to be 0·9166 fine, of French standard 0·900 fine. The legal weight of the sovereign is 0·2568 ounce of standard gold, or 123·274 grains; the weight coming from one pound of standard gold (5,760 grains) being coined into $44\frac{1}{2}$ guineas. Gold coins are legal tender to any amount, provided that the weight of each sovereign does not fall below 122·5 grains, or in the case of a half-sovereign 61·125 grains; these are the "least current" weights of the coins.

Note.—In analysis gold comes out among the sulphides of metals precipitated by sulphuretted hydrogen; and of those sulphides, it, like the sulphides of tin, antimony, and arsenium, is soluble in yellow sulphydrate of ammonium solution.

Quantivalence.—Gold is trivalent (Au''') in the auri- or auric compounds, univalent (Au') in the auro- or aurous salts.

REACTIONS.

Synthetical Reaction.—Place a fragment of gold (*e.g.* gold leaf) in ten or twenty drops of aqua regia (a mixture of three parts of nitric and four or five of hydrochloric acid), and set aside in a warm place; solution of perchloride of gold or auric chloride ($AuCl_3$) results. Evaporate nearly to dryness to remove most of the excess of acid, dilute with water, and retain the solution for subsequent experiments. Sixty grains of gold treated thus, and the resulting chloride dissolved in five ounces of distilled water, constitutes "Solution of Perchloride of Gold," B.P. The salt itself is very deliquescent. A compound of the chlorides of gold and sodium, in molecular proportions, crystallizes readily and is more stable.

$$Au_2 + 2HNO_3 + 6HCl = 2AuCl_3 + 2NO + 4H_2O.$$

This reaction has analytical interest also; for in examining a substance suspected to be or to contain metallic gold, solution would have to be effected in the above way before reagents could be applied. Gold is insoluble in hydrochloric nitric, and the weaker acids.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—Through a few drops of solution of an auric salt (the chloride, $AuCl_3$, is the only convenient one) pass sulphuretted hydrogen; a brown precipitate results (auric sulphide, Au_2S_3). Filter, wash, and add yellow sulphydrate of ammonium solution; the precipitate dissolves.

Second Analytical Reaction.—To solution of a salt of gold add a ferrous salt, and set the tube aside; metallic gold, having its characteristic lustrous appearance, is precipitated, a ferric salt remaining in solution. Oxalic acid, also, and most free metals, precipitate the gold.

This is a convenient way of preparing pure gold, or *fine gold*, as it is termed, or of working up the gold residues of laboratory operations. The precipitate, after boiling with hydrochloric acid, washing and drying, may be obtained in a button by mixing with an equal weight of borax or acid sulphate of potassium and fusing in a good furnace.

Third Analytical Reaction.—Add a few drops of dilute solutions of stannous and stannic chloride to a considerable quantity of distilled water; pour the liquid, a small quantity at a time, into a very dilute solution of auric chloride ($AuCl_3$), well stirring; the mixture assumes a purple tint, and flocks of a precipitate, known as the *Purple of Cassius* (from the name of the discoverer, M. Cassius), are produced.

The same compound is formed on immersing a piece of tin foil in solution of auric chloride; it is said to be a mixture of auric, aurous, stannic, and stannous oxides. It is the colouring agent in the finer varieties of ruby glass.

PLATINUM.

Symbol, Pt. Atomic weight, 194·4.

Source.—Platinum, like gold, occurs in nature in the free state, the chief sources of supply being Mexico, Brazil, and Siberia. It is separated from the soil by washing.

Uses.—The chief use of platinum is in the construction of foil, wire, crucibles, spatulas, capsules, evaporating-dishes, and stills, for the use of the chemical analyst or manufacturer. It is tolerably hard, fusible with very great difficulty, not dissolved by hydrochloric, nitric, or sulphuric acid, and only slightly affected by alkaline substances. It is attacked by aqua regia with production of perchloride of platinum or platinic chloride ($PtCl_4, 5H_2O$). It forms fusible alloys with lead and other metals, and with phosphorus a phosphide which easily melts. Neither of these substances, therefore, nor mixtures which may yield them, should be heated in platinum vessels. Hammered or chased, not drawn, vessels are the most durable. They are best cleaned by aid of a little fine water-worn (not "sharp") sea sand. They should not be very suddenly heated or very suddenly cooled. They should only be heated by the outer portions of flames, exposure to strongly heated carboniferous or siliconiferous surfaces being avoided, for at high temperatures platinum has a tendency to unite with carbon or silicon.

The chemical position of platinum among the elements is close to that of gold. Its atom is quadrivalent (Pt'''') in some compounds, in others apparently bivalent (Pt''). The higher salts are termed *platinic*, the lower *platinous*.

The specific gravity of platinum is 21·5; and that of *iridium*, an allied metal, 22·4.

REACTIONS.

Perchloride of Platinum. Platinic Chloride.

Synthetical Reaction.—Place a fragment of platinum in a little aqua regia, and set the vessel aside in a warm place, adding more acid from time to time if necessary; solution of perchloride of platinum ($PtCl_4$) results. Evaporate the solution to remove excess of acid, and complete the desiccation over a water-bath. Dissolve the residue in water, and retain the solution for subsequent experiments, and as a reagent for the precipitation of salts either of potassium or ammonium. A quarter of an ounce of platinum treated in this manner, and the resulting chloride dissolved in five ounces of water, forms "Solution of Perchloride of Platinum," B.P.

This reaction has analytical interest; for, in testing a substance suspected to contain metallic platinum, solution would have to be thus effected before reagents could be applied.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—Through a few drops of a solution of a platinic salt ($PtCl_4$ is the only convenient one), to which an equal quantity of solution of chloride of sodium has been added, pass sulphuretted hydrogen; a dark-brown precipitate results (platinic sulphide, PtS_2). Filter, wash, and add sulphydrate of ammonium; the precipitate dissolves.

If chloride of sodium be not present in the above reaction, the precipitated sulphide will contain platinous chloride, and may detonate if heated.

Second Analytical Reaction.—Add excess of carbonate of sodium and some sugar to solution of perchloride of platinum, and boil; a black precipitate (metallic platinum) falls.

Platinum black (B.P.) is the name of this precipitate. It possesses in a high degree a quality common to many substances, but largely possessed by platinum, namely, that of absorbing or *occluding* gases. In its ordinary state, after well washing and drying, it absorbs from the air and retains many times its bulk of oxygen. A drop of ether or alcohol placed on it is rapidly oxidized, the platinum becoming hot. This action may be prettily shown by pouring a few drops of ether into a beaker (one having portions of the top and sides broken off answers best), loosely covering the vessel with a card, and suspending within the beaker a platinum wire, one end being attached to the card by passing through its centre, the other terminating in a short coil or helix near the surface of the ether: on now warming the helix in a flame and then rapidly introducing it into the beaker, it will become red-hot and continue to glow. In this experiment partial combustion goes on between the ether vapour and the concentrated oxygen of the air, the products of the oxidation revealing themselves by their odour.

Third Analytical Reaction.—To solution of perchloride of platinum add solution of chloride of ammonium; a yellow granular precipitate (the double chloride, $PtCl_4, 2NH_4Cl$) falls. When slowly formed in dilute solutions, the precipitate is obtained in minute orange prisms.

Chloride of potassium (KCl) gives a similar precipitate ($PtCl_4$, $2KCl$). Platinic chloride having been stated to be a test for potassium and ammonium salts, the reader is prepared to find that potassium and ammonium salts are tests for platinic salts. The double sodium compound ($PtCl_4$,$2NaCl$) is soluble in water.

Collect the precipitate, dry, and heat in a small crucible; it is decomposed, and metal, in a finely divided grey state (*spongy platinum*), remains.

$$3\,(PtCl_4,\,2NH_4Cl) = Pt_3 + 2NH_4Cl + 16HCl + 2N_2.$$

Heat decomposes the salt of potassium into $Pt + 2KCl + Cl_4$, the chlorine escaping and the chloride of potassium remaining with the platinum.

In working up the platinum residues of laboratory operations, the mixture should be dried, burnt, boiled successively with hydrochloric acid, water, nitric acid, water, then dissolved in aqua regia, excess of acid removed by evaporation, chloride of ammonium added, the precipitate washed with water, dried, ignited, and the resulting spongy platinum retained or converted into perchloride for use as a reagent for alkali-metals. It is by such processes that the native platinum is treated to free it from the rare metals palladium, rhodium, osmium, ruthenium, and iridium. The spongy platinum is converted into the massive condition by a refinement on the blacksmith's process of *welding* (German *wellen*, to join); or by fusing in a flame of pure oxygen and hydrogen gases—the oxyhydrogen blowpipe.

Occlusion by spongy platinum.—Spongy platinum has great power of occlusion. A small piece held in a jet of hydrogen causes ignition of the gas, owing to the close approximation of particles of oxygen (from the air) and hydrogen. Dobereiner's lamp is constructed on this principle—the apparatus being essentially a vessel in which hydrogen is generated by the action of diluted sulphuric acid on zinc, and a cage for holding the spongy platinum.

CADMIUM.

Symbol, Cd. Atomic weight, 112.

In most of its chemical relations cadmium resembles zinc. In nature it occurs chiefly as an occasional constituent of the ore of that metal. In distilling zinc containing cadmium, the latter, being the more volatile, passes over first. In analytical operations cadmium, unlike zinc, comes down among the metals precipitated by sulphuretted hydrogen; that is, its sulphide is insoluble in diluted hydrochloric acid, while sulphide of zinc is soluble. It is a white malleable metal, nearly as volatile as mercury. Sp. gr. 8·7.

Beyond the occasional employment of the sulphide as a pigment (*jaune brilliant*), and the iodide in photography, cadmium and its salts are but little used. The atom of cadmium is bivalent (Cd″).

REACTIONS.

Iodide of Cadmium.

Synthetical Reaction.—Digest together, in a flask, metallic cadmium, warm water, and iodine, until the colour of the iodine disappears; solution of iodide of cadmium (CdI_2) remains. Pearly micaceous crystals may be obtained on evaporating the solution.

This salt is employed with other iodides in iodizing collodion for photographic use. It readily melts, and is soluble in water or spirit, the solution reddening litmus.

First Analytical Reaction.—Through solution of a cadmium salt (CdI_2 or $CdCl_2$) pass sulphuretted hydrogen; a yellow precipitate (sulphide of cadmium, CdS) falls, resembling in appearance arsenious, arsenic, and stannic sulphides. Add sulphydrate of ammonium; the precipitate, unlike the sulphides just mentioned, does not dissolve.

Sulphides of cadmium and copper may be separated by solution of cyanide of potassium, in which sulphide of copper is soluble and sulphide of cadmium insoluble.

Second Analytical Reaction.—To a cadmium solution add solution of potash; a white precipitate results (hydrate of cadmium, Cd2HO), insoluble in excess of the potash.

Hydrate of zinc (Zn2HO), precipitated under similar circumstances, is soluble in solution of potash; the filtrate from the hydrate of cadmium may therefore be tested for any zinc occurring as an impurity by applying the appropriate reagent—sulphydrate of ammonium.

Before the blowpipe-flame, on charcoal, cadmium salts give a brown deposit (oxide of cadmium, CdO).

BISMUTH.

Symbol, Bi. Atomic weight, 208.

Source.—Bismuth occurs in the metallic state in nature. It is freed from adherent quartz, etc., by simply heating, when the metal melts, runs off, and is collected in appropriate vessels (*Bismuthum*, B.P.). It is also met with in combination with other elements. Bismuth is greyish white with a distinct pinkish tinge.

Purification.—Arsenium may be removed from melted bismuth by a rod of iron, arsenide of iron rising to the surface of the mass: antimony by stirring in some oxide of bismuth, when oxide of antimony separates. Other metals in bismuth, especially copper, are converted into sulphides, while bismuth is not affected, on fusing the crude metal with about five per cent. of cyanide of potassium, and two per cent. of sulphur, the whole being well stirred for a quarter of an hour with a clay rod (stem of a tobacco-pipe). On pouring off the metal from the flux, and melting and stirring it with about five per cent. of a mixture of the carbonates of potassium and sodium, sulphur and traces of other impurities are removed, and the metal is obtained pure (*Bismuthum Purificatum*, B.P.).—*Tamm.*

Uses.—Beyond the employment of some of its compounds in medicine, bismuth is but little used. Melted bismuth expands considerably on solidifying, and hence is valuable in taking sharp impressions of dies. It is a constituent of some kinds of type-metal and of pewter-solder.

The position of bismuth among the metals is close to that of arsenium and antimony. Its atom is trivalent (Bi''') and, rarely, quinquivalent (Bi^{v}).

REACTIONS HAVING SYNTHETICAL INTEREST.

Nitrate of Bismuth.

First Synthetical Reaction.—To a few drops of nitric acid and an equal quantity of water, in a test-tube, add a little powdered bismuth, heating the mixture if necessary; nitric oxide (NO) escapes, and solution of *nitrate of bismuth* ($Bi3NO_3$) results.

$$\underset{\text{Bismuth.}}{Bi_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Nitrate of bismuth.}}{2(Bi3NO_3)} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

The solution evaporated gives crystals ($Bi3NO_3,5H_2O$), any arsenium which the bismuth might contain remaining in the mother-liquor.

To make *nitrate* of bismuth and other salts on a larger scale, 2 ounces of the metal, in small fragments, are gradually added to a mixture of 4 fluid ounces of nitric acid and 3 of water, and, when effervescence (due to escape of nitric oxide) has ceased, the mixture is heated for ten minutes, poured off from any insoluble matter, evaporated to 2 fluid ounces to remove excess of acid, and then either set aside for *crystals* to form, or poured into half a gallon of water to form the *oxynitrate* of bismuth, or into a solution of 6 ounces of carbonate of ammonium in a quart of water to form the *oxycarbonate* as described in the following reactions.

The precipitates should be washed with cold water and dried at a temperature not exceeding 150° F. Exposed in the moist state to 212° for any length of time, they undergo slight decomposition.

Subnitrate or Oxynitrate of Bismuth.

Second Synthetical Reaction.—Pour some of the above solution of nitrate into a considerable quantity of water; decomposition occurs, and oxynitrate of bismuth ($BiONO_3$) in a hydrous state ($BiONO_3$, H_2O) (*Bismuthi Subnitras*, B.P.) is precipitated:—

$$\underset{\text{Nitrate of bismuth.}}{Bi3NO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Oxynitrate of bismuth.}}{BiONO_3} + \underset{\text{Nitric acid.}}{2HNO_3}$$

Filter, and test the filtrate for bismuth by adding excess of carbonate of sodium; a precipitate shows that some bismuth remains in solution. The following equation, therefore, probably more nearly represents the decomposition:—

$$\underset{\substack{\text{Nitrate of}\\\text{bismuth.}}}{5(Bi3NO_3)} + \underset{\text{Water.}}{8H_2O} = \underset{\substack{\text{Oxynitrate of}\\\text{bismuth.}}}{4(BiONO_3, H_2O)} + \underset{\substack{\text{Nitrate of bismuth}\\\text{in acid.}}}{Bi3NO_3; 8HNO_3}$$

Decomposition of nitrate of bismuth by water is the process of the British Pharmacopœia for the preparation of oxynitrate or "subnitrate" of bismuth for use in medicine. For this purpose the original metal must contain no arsenium. In manufacturing the compound, therefore, before pouring the solution of nitrate into water, the liquid should be tested for arsenium by one of the hydrogen tests; if that element be present, the solution must be evaporated, and only the deposited crystals be used in the preparation of the oxynitrate. For on pouring an arsenical solution of nitrate of bismuth into water, the arsenium is not wholly removed in the supernatant liquid, unless the oxynitrate be redissolved and reprecipitated several times, according to the amount of arsenium present.

Subnitrate of bismuth is gradually decomposed by solution of alkaline carbonates; also by the bicarbonates with production of carbonic acid gas; oxycarbonate of bismuth and nitrate of the alkali-metal being formed. It is sometimes administered in the form of a lozenge (*Trochisci Bismuthi*, B.P.).

Oxysalts of Bismuth.—It will be noticed that the formula for subnitrate of bismuth ($BiNO_4$) does not accord with that of other nitrates, the characteristic elements of which are NO_3. Analogy would seem to indicate, however, that the fourth atom of oxygen has different functions to the three in the NO_3; for on pouring solution of chloride of bismuth ($BiCl_3$) into water, oxychloride is produced ($BiOCl$) (a white powder used as a cosmetic, "pearl-white" (*Blanc de Perle*), also in enamels and in some varieties of sealing-wax). The bromide ($BiBr_3$) and iodide (BiI_3), similarly treated, yield oxybromide ($BiOBr$) and oxyiodide ($BiOI$). The subnitrate ($BiNO_4$) is, therefore, probably an analogous compound, an oxynitrate ($BiONO_3$). The sulphate (Bi_23SO_4) also decomposes when placed in water, giving what may be termed an oxysulphate, the formula of which is $Bi_2O_2SO_4$.

It is difficult to prove whether or not the water in the "subnitrate" or hydrous oxynitrate of bismuth ($BiONO_3, H_2O$) is an integral part of the salt. If it is, the compound is simply the hydrato-nitrate ($BiNO_32HO$) of bismuth.

Oxide of Bismuth.

Third Synthetical Reaction.—Boil subnitrate of bismuth with solution of soda for a few minutes; it is converted into yellowish oxide of bismuth (Bi_2O_3) (*Bismuthi Oxidum*, B.P.).

$$\underset{\substack{\text{Oxynitrate of}\\ \text{bismuth.}}}{2BiONO_3} + \underset{\substack{\text{Hydrate of}\\ \text{sodium.}}}{2NaHO} = \underset{\substack{\text{Oxide of}\\ \text{bismuth.}}}{Bi_2O_3} + \underset{\substack{\text{Nitrate of}\\ \text{sodium.}}}{2NaNO_3} + \underset{\text{Water.}}{H_2O}$$

Subcarbonate or Oxycarbonate of Bismuth.

Fourth Synthetical Reaction.—To solution of nitrate of bismuth add solution of carbonate of ammonium; a white precipitate of hydrous oxycarbonate ($2Bi_2O_2CO_3,H_2O$) (*Bismuthi Carbonas*, B.P.) falls.

$$\underset{\text{Nitrate of bismuth.}}{2(Bi3NO_3)} + \underset{\text{"Carbonate" of ammonium.}}{2N_3H_{11}C_2O_5} + H_2O = \underset{\text{Nitrate of ammonium.}}{6NH_4NO_3} + \underset{\text{Oxycarbonate of bismuth.}}{Bi_2O_2CO_3} + \underset{\text{Carbonic acid gas.}}{3CO_2}$$

This compound may be regarded as similar in constitution to the oxysalts just described. In Bi_2CO_5 one scarcely recognises the characteristic elements of carbonates; but considering the preparation to be an oxycarbonate ($Bi_2O_2CO_3$), its relations to carbonates and oxides are evident. These subsalts may all be viewed as normal bismuth salts in one molecule of which an atom of oxygen displaces an equivalent proportion of other acidulous atoms or radicals :—

Chloride	$Bi3Cl$	Oxychloride . .	$BiOCl$
Bromide	$Bi3Br$	Oxybromide . .	$BiOBr$
Iodide	$Bi3I$	Oxyiodide . . .	$BiOI$
Nitrate	$Bi3NO_3$	Oxynitrate . .	$BiONO_3$
Sulphate	Bi_23SO_4	Oxysulphate . .	$Bi_2O_2SO_4$
Carbonate (unknown)	Bi_23CO_3	Oxycarbonate .	$Bi_2O_2CO_3$

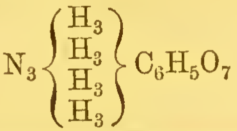
They may be viewed, in short, as salts in process of conversion to oxide; continue the substitution further, and each yields oxide of bismuth (Bi_2O_3). They are also regarded as salts of a hypothetical radical bismuthyl (BiO).

Citrate of Bismuth.

Fifth Synthetical Reaction.—To a nitric solution of nitrate of bismuth add water with frequent shaking until a slight cloudiness of oxynitrate remains; then add solution of citrate of sodium; warm and stir the mixture; set aside to cool; collect on a filter, wash, and dry the precipitated citrate of bismuth (*Bismuthi Citras*, B.P.), $BiC_6H_5O_7$.

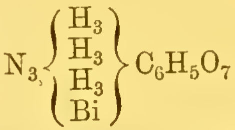
$$\underset{\text{Nitrate of bismuth.}}{Bi3NO_3} + \underset{\text{Citrate of sodium.}}{Na_3C_6H_5O_7} = \underset{\text{Citrate of bismuth.}}{BiC_6H_5O_7} + \underset{\text{Nitrate of sodium.}}{3NaNO_3}$$

Sixth Synthetical Reaction.—To citrate of bismuth rubbed to a paste with a very little water, add sufficient solution of ammonia to dissolve the citrate. The product, when of a strength of 800 grains of citrate in a pint, is the official Solution of Citrate of Bismuth and Ammonium (*Liquor Bismuthi* *et Ammonii Citratis*, B.P.), shortly termed *Liquor Bismuthi*. This solution, evaporated to the consistence of syrup, spread on glass, and dried at 100° F., yields scales of the solid salt (*Bismuthi et Ammonii Citras*, B.P.). In constitution it is possibly ordinary citrate of ammonium, in which three atoms of hydrogen are displaced by one of bismuth. (For similar salts, see p. 237.)



$$N_3\left\{\begin{matrix}H_3\\H_3\\H_3\\H_3\end{matrix}\right\}C_6H_5O_7$$

Citrate of hydrogen-ammonium.



$$N_3\left\{\begin{matrix}H_3\\H_3\\H_3\\Bi\end{matrix}\right\}C_6H_5O_7$$

Citrate of bismuth-ammonium.

REACTIONS HAVING ANALYTICAL INTEREST (TESTS).

First Analytical Reaction.—Through solution of a bismuth salt (a slightly acid solution of nitrate, for example) pass sulphuretted hydrogen; a black precipitate (sulphide of bismuth, Bi_2S_3) falls. Add ammonia (to neutralize acid) and then sulphydrate of ammonium; the precipitate, unlike As_2S_3 and Sb_2S_3, is insoluble.

Second Analytical Reaction.—Concentrate almost any acid solution of a bismuth salt and pour into much water (containing chloride of sodium); a white precipitate results.

This reaction is characteristic of bismuth salts: it has already been amply explained. The oxychloride is specially insoluble, and is distinguished from that of antimony by being insoluble in solution of tartaric acid.

Third Analytical Reaction.—To a solution of bismuth salt add an alkali; a white precipitate results (hydrate of bismuth, Bi3HO), insoluble in excess, and becoming yellowish on boiling.

Fourth Analytical Reaction.—A small quantity of the following reagent, including both supernatant liquid and precipitated yellow scales, is transferred to a test-tube, and gradually heated till solution takes place. Any liquid containing, or supposed to contain, bismuth is then added, and the whole allowed to cool. The separated scales will show a distinct change in colour from the original yellow to dark orange or crimson, according to the quantity of bismuth present.

The reagent may be prepared by adding to a boiling solution of acetate of lead, containing about $\frac{1}{2}$ gr. to the ounce, a few drops of acetic acid, and solution of iodide of potassium in considerable excess. On cooling, iodide of lead is deposited in the characteristic yellow crystalline plates or scales.

Test for phosphate of calcium in bismuth salts.—Dissolve the powder in nitric acid, add about twice its weight of citric acid and sufficient ammonia to give decided alkalinity; then boil, keeping the mixture faintly alkaline with ammonia, bismuth remains in solution, and phosphate of calcium is precipitated.

Official Tests for other impurities in bismuth or its salts.—Dissolve in nitric acid; concentrate and set aside for crystals of nitrate of bismuth to form; pour off the mother-liquor, which will contain any impurities in a concentrated form. If this mother-liquor be evaporated with hydrochloric acid until all the nitric acid is dissipated, a little of the product yields no evidence of arsenium on being examined by the hydrogen test, commonly known as Marsh's test; no blue coloration on adding water and excess of ammonia (copper), and no precipitate on filtering and saturating the ammoniacal filtrate with nitric acid (silver); no white precipitate with diluted sulphuric acid (lead); no red or black precipitate with sulphite of sodium (tellurium or selenium); and no blue precipitate with ferrocyanide of potassium (iron).

THE READER IS AGAIN ADVISED TO TRACE OUT THE EXACT NATURE OF EACH OF THE FOREGOING REACTIONS, CHIEFLY BY AID OF EQUATIONS OR DIAGRAMS.

QUESTIONS AND EXERCISES.

Enumerate the fifteen metals, salts of which are frequently employed in pharmacy.—Mention the twelve rarer metals interesting to pharmacists.—Name the sources and official compounds of lithium.—Explain the formation of citrate of lithium.—What is the strength of *Liquor Lithiæ Effervescens*?—On what chemical hypothesis are lithium compounds administered to gouty patients?—Describe the relation of lithium to other metals.—What is the chief test for lithium?—Write a paragraph on strontium, its natural compounds, chemical relations, technical applications, and tests.—What are the formula and properties of oxalate of cerium?—Name the commonest ore of manganese; and give an equation descriptive of its reaction with hydrochloric acid.—Explain the formation of permanganate of potassium, employing diagrams or equations.—How do the manganates of potassium act as disinfectants?—What are the chief tests for manganese?—What are the chief uses of the compounds of cobalt?—How is cobalt analytically distinguished from nickel?—Mention applications of nickel in the arts.—What is the general colour of nickel salts?—State the method of preparation of red chromate of potassium.—Give the formulæ of red and yellow chromates of potassium.—How is red chromate of potassium obtained?—Describe the action of sulphuretted hydrogen on acidified solutions of chromates.—What is the formula of chrome alum?—Mention the chief tests for the chromic radical, and for chromium.—How would you detect iron, chromium, and aluminium, in a solution?—Define *tinstone*, *stream-tin*, *block-tin*, *grain-tin*, *tin plate*.—Describe the position occupied by tin in relation to other metals.—What is the difference between stannic acid and metastannic acid?—State the applications of tin in the arts.—Mention the chief tests for stannous and stannic salts.—Name the best antidote in cases of poisoning by tin solutions.—How is gold dust separated from the earthy matter with which it is naturally associated?—How much pure gold do English coin and jewellers' gold contain?—State the average thickness of gold leaf.—What is the weight of a sovereign?—Explain the term "fineness" as applied to gold.—What effect is produced on gold by hydrochloric, nitric, and nitrohydrochloric acids respectively?—By what reagents may metallic gold be precipitated from solution?—How is "purple of Cassius" prepared?—Whence is platinum obtained?—Why are platinum utensils peculiarly adapted for use in chemical laboratories? How is perchloride of platinum prepared?—Name the chief tests for platinum.—What is "platinum black"?—Describe an experiment demonstrative of the large amount of attraction for gases possessed by metallic platinum.—How is "spongy platinum" produced?—By what process may platinum be recovered from residues?—What is *occlusion* in Chemistry?—In what condition does cadmium occur in Nature?—By what process may iodide of cadmium be prepared?—Mention the chief test for cadmium.—Distinguish sulphide of cadmium from sulphides of similar colour.—How is cadmium separated from zinc?—How does bismuth occur in Nature?—What is the quantivalence of bismuth?—Write down equations descriptive of the action of nitric acid on bismuth, and water on nitrate of bismuth.—How may arsenium be excluded from bismuth salts?—Give a diagram of the official process for carbonate of bismuth.—Write formulæ showing the accordance in molecular constitution of the official subnitrate and carbonate with the other salts of bismuth, and with ordinary nitrates and carbonates.—How is *Liquor Bismuthi et Ammonii Citratis* prepared?—Mention the tests for bismuth.

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ONE OF THE COMMON AND RARER METALS HITHERTO CONSIDERED.

Add hydrochloric acid.

<table>
<tr>
<td rowspan="6">Precipitate
Hg(ous) Pb Ag.
Collect, wash, and add NH_4HO.
Hg ppt., blackened.
Pb ppt., still white.
Ag ppt., dissolved.
Sb and Bi may also be precipitated by HCl, but are dissolved on adding more HCl.</td>
<td colspan="7">If HCl gave no precipitate, the metal is still in the liquid: pass H_2S through the solution.</td>
</tr>
<tr>
<td rowspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb
Sn Au Pt.
Collect, wash, add NH_4HS.
Insoluble.
Cd, yellow
Cu
Hg(ic)
Pb
Bi } black.
Soluble.
As (ous&ic).
Sn(ic) } yellow
Sb, orange
Sn(ous)
Au
Pt } black
Apply special tests for each to the original solution. For these *see* the previous pages.</td>
<td colspan="6">If H_2S gave no precipitate, add NH_4Cl, NH_4HO, and NH_4HS.</td>
</tr>
<tr>
<td rowspan="4">Precipitate.
Zn Mn Co Ni Al
Fe Cr
Zn
Al } white
Cr, green.
Mn, skin-tint.
Ni
Co
Fe } black.
Test specially for each in original solution. *See* previous pages.</td>
<td colspan="5">If NH_4HS gave no precipitate, add $(NH_4)_2CO_3$.</td>
</tr>
<tr>
<td colspan="3">Precipitate.
Ba Sr Ca
Collect, wash, dissolve in $HC_2H_3O_2$, add K_2CrO_4.</td>
<td colspan="2">If $(NH_4)_2CO_3$ gave no precipitate, add $(NH_4)_2HAsO_4$.</td>
</tr>
<tr>
<td rowspan="2">Ppt.
Ba.</td>
<td colspan="2">Sol.
Sr Ca
Add dil. H_2SO_4.</td>
<td rowspan="2">Ppt.
Mg.</td>
<td rowspan="2">If no precipitate, test original solution in flame on loop of Pt. wire.
L, crimson.
Na, yellow.
K, violet.
If neither, test orig.sol.for NH_4.</td>
</tr>
<tr>
<td>Ppt.
Sr.</td>
<td>Sol.
Ca.</td>
</tr>
</table>

The Analytical Classification of Metals.
Practical Analysis.

Bismuth is the last of the metals whose synthetical or analytical relations are of general interest. The position of the rarer among the common metals, and the influence which either has on the other during the manipulations of analysis, will now be considered. These objects will be best accomplished, and a more intimate acquaintance with all the

OUTLINE OF THE ANNEXED ANALYTICAL TABLES.

HCl	H_2S		NH_4HS		$(NH_4)_2CO_3$	$(NH_4)_2$ $HAsO_4$	
Hg (as mercurous salt)	Cd	Insoluble in NH_4HS.	Zn	Hydrates soluble in NH_4HO.	Ba	Mg	K
	Cu		M *		Sr		Na
Pb (partially)	Hg (as mercuric salt)		Co		Ca		NH_4
Ag	Pb (entirely)		Ni				
	Bi		Al	Hydrates insol. in NH_4HO.		L	
	As (as arsenious or arsenic salt)	Soluble in NH_4HS.	Fe				
	Sb		Cr				
	Sn (as stannous or stannic salt)						
	Au						
	Pt						

* *See* p. 268.

Note.—The laboratory student should practice the examination of aqueous solutions of salts of the above metals until he is able to analyse with facility and accuracy.

TABLE OF SHORT DIRECTIONS FOR APPLYING SOME OF THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS OR ONLY SLIGHTLY ACID SOLUTION OF ORDINARY SALTS OF ANY OF THE COMMON OR RARER METALS OF GENERAL INTEREST.

Add hydrochloric acid.

<table>
<tr><td colspan="3">Precipitate
Hg(ous) Pb Ag.
Wash, boil with water, filter.</td><td colspan="20">Filtrate
Cd Cu Hg(ic) Pb Bi As(ous)(ic) Sb Sn(ous)(ic) Zn Mn Co Ni Al Fe(ous)(ic) Cr Ba Ca Sr Mg L K Na NH_4.
Pass H_2S through the liquid, filter.</td></tr>
<tr><td colspan="2">Precipitate
Hg(ous) Ag.
Wash, add NH_4HO.</td><td rowspan="5">Filtrate
Pb.
Add H_2SO_4.
White ppt.</td><td colspan="8">Precipitate
Cd Cu Hg(ic) Pb Bi As Sb Sn.
Collect, wash, digest in NH_4HS, filter.</td><td colspan="12">Filtrate
Zn Mn Co Ni Al Fe Cr Ba Ca Sr Mg L K Na NH_4.
Add NH_4Cl, NH_4HO, and NH_4HS, warm gently, and filter.</td></tr>
<tr><td rowspan="4">Ppt.
Hg.
(ous).
Black.</td><td rowspan="4">Filtrate
Ag.
Add an acid.
White ppt.</td><td colspan="5">Precipitate
Cd Cu Hg(ic) Pb Bi.
Wash, boil in HNO_3, filter.</td><td colspan="3">Filtrate
As Sb Sn.
Add dilute HCl, filter, drain well, add *strong* HCl, boil, dilute slightly, filter.</td><td colspan="6">Precipitate
Zn Mn Co Ni Al Fe Cr.
Collect, wash, dissolve in HCl, with a few drops of HNO_3, boil, add NH_4HO, stir, filter.</td><td colspan="6">Filtrate
Ba Ca Sr Mg L K Na NH_4.
Add $(NH_4)_2CO_3$, warm, filter.</td></tr>
<tr><td rowspan="3">Ppt.
Hg.
(ic)
Black.
Confirm by Cu test in original solution.</td><td colspan="4">Filtrate
Cd Cu Pb Bi.
Add NH_4HO, filter.</td><td rowspan="3">Insol.
As.
Yellow. Confirm by Fleitmann's test.</td><td colspan="2">Filtrate
Sn Sb.
Pour into H-apparatus.</td><td colspan="3">Precipitate*
Fe Al Cr.
Wash, dry, fuse on foil with Na_2CO_3 and KNO_3, boil in water, and filter.</td><td colspan="3">Filtrate
Zn Mn Co Ni.
Acidify with $HC_2H_3O_2$, pass H_2S, filter.</td><td colspan="3">Precipitate.
Ba Sr Ca.
Collect, wash, dissolve in $HC_2H_3O_2$, add excess of K_2CrO_4, filter.</td><td colspan="3">Filtrate
Mg L K Na NH_4,
Add $(NH_4)_2HAsO_4$, stir, filter.</td></tr>
<tr><td colspan="2">Precipitate
Pb Bi.
Wash, add a few drops HNO_3, dilute, filter.</td><td colspan="2">Filtrate
Cd Cu.
Add KCy and H_2S.</td><td rowspan="2">Sn
remains on Zn.
Dissolve in HCl, and apply tests.</td><td rowspan="2">Sb
escapes as SbH_3.
Test as usual.</td><td rowspan="2">Residue
Fe_2O_3, brown.
Test original solution for ferrous or ferric state.</td><td colspan="2">Filtrate
If yellow, Cr present.
Divide into two parts.</td><td rowspan="2">Sol.
Mn.
Add NH_4HO and NH_4HS. Pink, turning brown.
Search also for Mn in the Fe Al Cr ppt.</td><td colspan="2">Precipitate
Zn Co Ni.
Boil with HCl and a little HNO_3; add KHO, filter.</td><td rowspan="2">Ppt.
Ba.
Yellow.</td><td colspan="2">Filtrate
Sr Ca.
Add dilute H_2SO_4, let stand, filter.</td><td rowspan="2">Ppt.
Mg.
White</td><td colspan="2">Filtrate
L K Na NH_4.
Evaporate to small bulk, add NH_4HO.</td></tr>
<tr><td>Ppt.
Bi.
White.</td><td>Filt.
Pb.
Dilute, add H_2SO_4, set aside; white ppt.</td><td>Ppt.
Cd.
Yellow.</td><td>Filt.
Cu.
Acidify with $HC_2H_3O_2$ Brown ppt.</td><td>Sol.
Al.
Add NH_4Cl and warm. White ppt.</td><td>Sol.
Cr.
Add $HC_2H_3O_2$ and excess of $AgNO_3$; red ppt. Or boil with H_2SO_4 & spirit. Greensol.</td><td>Filt.
Zn.
Add NH_4HS. White ppt.</td><td>Precipitate.
Co Ni.
Dissolve in HCl. and proceed as directed on p.272</td><td>Ppt.
Sr.
White</td><td>Filt.
Ca.
Add NH_4HO and $(NH_4)_2C_2O_4$ white ppt.</td><td>Ppt.
L.
See p. 303.</td><td>Filtrate
K Na NH_4.
Evaporate, ignite, dissolve.
K by $PtCl_4$.
Na by flame,
NH_4 in original solution.</td></tr>
<tr><td colspan="3">*See* also p. 300.</td><td colspan="5">*See* also pp. 300 and 301.</td><td colspan="3">*See* also p. 300.
Au and Pt are specially sought when necessary.</td><td colspan="3">*See* also p. 302.
* Test this also for Mn by Crum's process, p. 268.</td><td colspan="3"></td><td colspan="3">*See* also page 302.</td><td colspan="3"></td></tr>
</table>

To face p. 298.]

metals be obtained, by analysing, or studying the methods of analysing, solutions containing one or more metallic salts.

Of the foregoing Tables, the first includes directions for the analysis of an aqueous or only slightly acid solution containing but one salt of any of the metals hitherto considered. Here the colour of the precipitate or precipitates afforded by a metal under given circumstances must largely be relied on in attempting the detection of the various elements.

The long Table is intended as a chart for the analysis of solutions containing salts of more than one of the common and rarer metals. It is a compilation from the foregoing reactions—an extension of the scheme for the analysis of salts of the ordinary metals. It often may be altered or varied in arrangement to suit the requirements of the analyst.

That on p. 298 is a mere outline of the other two Tables. It gives the position of the metals in relation to each other, and will much aid the memory in recollecting that relation.

The analysis of solutions containing only one metal will, as already stated, serve to impress the memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles. Medical students and junior pharmaceutical students seldom have time to go farther than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all of the members of a group (*see* previous pages), then examining solutions containing more than one group, and finally analysing liquids in which are dissolved several salts of any of the common or rarer metals.

The Author cannot too strongly recommend students thoroughly to master the art of analysis, not only on account of its direct value, but because its practice enables the learner rapidly and soundly to acquire a good knowledge of Chemistry, and greatly to improve his general mental faculties.

GENERAL AND SPECIAL MEMORANDA RELATING TO THE PRECEDING ANALYTICAL TABLES.

General Memoranda.

These charts are constructed for the analysis of salts more or less soluble in water.——The student has still to learn how substances insoluble in water are to be brought into a state of solution; but, once dissolved, their analysis is effected by the same scheme as that just given. The Tables, especially the longer, folded one, may therefore be regarded as fairly representing the method by which metallic constituents of chemical substances are separated from each other and recognised.——The methods of isolation of the complementary constituent of the salt (the reactions of non-metals and acidulous radicals) will form the next object of practical study.

The general memoranda given in connection with the first Table (p. 255) are equally applicable to this extended second Table, and should again carefully be read through.

Special Memoranda.

The hydrochloric-acid precipitate may at first include some antimony and bismuth as oxychlorides, readily dissolved, however, by excess of acid.——If either of these elements be present, the washings of the precipitate will probably be milky; in that case add a few drops of hydrochloric acid, which will clear the liquid and make way for the application of the test for lead.

The sulphuretted-hydrogen precipitate may be white, in which case it is nothing but sulphur; for, as already indicated, ferric salts are reduced to ferrous, and chromates to the lower salts of chromium, by sulphuretted hydrogen, finely divided, and, therefore, whitish sulphur being deposited:—

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2;$$

$$4H_2CrO_4 + 6H_2S + 12HCl = 2Cr_2Cl_6 + 16H_2O + 3S_2.$$

But the precipitate may also be coloured, or even white when only lead or mercury is present, through an insufficiency of sulphuretted hydrogen having produced oxysulphide or hydrato-sulphide, etc. The gas should be passed through the liquid until, even after well shaking, the latter smells strongly of sulphuretted hydrogen.

The portion of the sulphuretted-hydrogen precipitate dissolved by sulphydrate of ammonium may include a trace of copper, sulphide of copper being not altogether insoluble in sulphydrate of ammonium.——On adding hydrochloric acid to the sulphydrate-of-ammonium solution, a white precipitate of sulphur only may be precipitated, the sulphydrate of ammonium nearly always containing free sulphur.——Strong hydrochloric acid does not readily dissolve small quantities of sulphide of antimony out of much sulphide of arsenium; and, on the other hand, the strong hydrochloric acid takes into solution a small quantity of sulphide of arsenium if much sulphide of antimony be present. The precipitates or the original solutions should therefore be examined by the other (hydrogen) tests for these elements if doubt exist concerning the presence or absence of either. Tin remains in the hydrogen-bottle in the metallic state, deposited as a black powder on the zinc used in the experiment. The contents of the bottle are turned out into a dish, ebullition continued until evolution of hydrogen ceases, and the zinc is taken up by the excess of sulphuric acid employed; any tin is then filtered out, washed, dissolved in a few drops of hydrochloric acid, and the liquid tested for tin by the usual reagents.——Tin may be detected in the mixed sulphides of tin, arsenium, and antimony by the blowpipe reaction (p. 280).

The portion of the sulphuretted-hydrogen precipitate not dissolved by the sulphydrate of ammonium may leave a yellow semi-fused globule of sulphur on boiling with nitric acid. This globule may be black, not only from presence of mercuric sulphide, but also from enclosed particles of other sulphides protected by the sulphur from the action of the acid. It may also contain sulphate of lead, produced by the action of nitric acid on sulphide of lead. In cases of doubt the mass must be removed from the liquid, boiled with nitric acid till dissolved, the solution evaporated to remove excess of acid, and the residue examined; but usually it may be disregarded.——Before testing for bismuth, any considerable excess of acid should be removed by evaporation, and the residual liquid should be freely diluted. If no precipitate (oxynitrate of bismuth) appear, chloride-of-ammonium solution may be added, oxychloride of bismuth more readily forming than even oxynitrate.——Or any nitric acid or sulphuric acid having been neutralized by ammonia, hydrochloric acid is added and then iodide of potassium; a rich orange colour results if bismuth be present.——Bismuth may also be detected in the mixed precipitated hydrates of bismuth and lead, obtained in the ordinary course of analysis, by dissolving a portion of the precipitate in acetic acid, and adding the liquid to the hot iodide of lead solution mentioned in the reactions for bismuth (p. 294).——In testing for lead by sulphuric acid, the liquid should be diluted and set aside for some time.

Mercury may also be isolated by digesting the sulphuretted-hydrogen precipitate in sulphydrate of sodium instead of sulphydrate of ammonium. The sulphides of arsenium, antimony, tin, and mercury are thus dissolved out. The mixture is then filtered, excess of hydrochloric acid added to the filtrate, and the precipitated sulphides collected on a filter, washed, and digested in sulphydrate of ammonium; sulphide of mercury remains insoluble, while the sulphides of arsenium, antimony, and tin are dissolved. By this method copper also appears in its right place only, sulphide of copper being insoluble in sulphydrate of sodium. The other metals are then separated in the usual way.

The sulphydrate-of-ammonium precipitate may, if the original solution was acid, contain Phosphates, Oxalates, Silicates, and Borates of Barium, Calcium, and Magnesium. These will subsequently come out with the iron, and, being white, give the iron precipitate a light-coloured appearance; their examination must be conducted separately, by a method described subsequently in connection with the treatment of substances insoluble in water.——The precipitate containing aluminium, iron, and chromium hydrates often contains some manganese. This manganese may be detected by washing the hydrates to remove all trace of chlorides, boiling with nitric acid, adding either puce-coloured oxide of lead or red lead, and setting the vessel aside; if manganese be present, a red or purple liquid is produced.——Sulphide of nickel is not easily removed by filtration (*vide* p. 271) until most of the excess of sulphydrate of ammonium has been dissipated by prolonged ebullition.

The carbonate-of-ammonium precipitate may not contain the whole of the barium, strontium, and calcium in the mixture, unless free ammonia be present; for the carbonates of those metals are soluble in water charged with carbonic acid. If, therefore, the liquid is not distinctly ammoniacal, solution of ammonia should be added.——Neither carbonate nor hydrate of ammonium wholly precipitates magnesian salts; and as partial precipitation is undesirable, a solvent, in the form of an alkaline salt (chloride of ammonium), if not already in the liquid, should be added.——In the chart opposite p. 298, strontium is ordered to be separated from calcium by adding to the acetic solution diluted sulphuric acid. The latter, unless extremely dilute, may precipitate calcium. Any such loss of calcium is in itself of little consequence, because enough sulphate of calcium remains in the filtrate to afford a calcium reaction when ammonia and oxalate of ammonium are subsequently added. But the calcium precipitated by the sulphuric acid may be wrongly set down as strontium. Therefore test a little of the acetic solution for strontium by an aqueous solution of sulphate of calcium, when, if no precipitate falls after setting aside for several minutes, strontium may be regarded as absent. If a precipitate occurs, strontium is present: the rest of the acetic solution is then tested for calcium as directed in the chart, the final testing by oxalate of ammonium being, of course, preceded by the addition of ammonia.——Barium may be overlooked if oxidation happens to have converted any sulphur into sulphuric acid.

Lithium.—The search for lithium may usually be omitted. Should a precipitate, supposed to be due to lithium, be obtained, it must be tested in a flame (=scarlet tint), as a little magnesium not infrequently shows itself under similar circumstances.

Spectral Analysis.—If present only in minute proportions, the lithium may also remain with the alkalies; it can then only be detected by physical analysis (by a prism) of the light emitted from a tinged flame—by, in short, an instrument termed a spectroscope. Such a method of examination is called spectral analysis, a subject of much interest and of no great difficulty, but scarcely within the range of medical or pharmaceutical students; it will be described briefly in connection with the methods of analysing solid substances.

QUESTIONS AND EXERCISES.

Describe a general method of analysis by which the metal of a single salt in a solution could be quickly detected.—Give illustrations of black, white, light-pink, yellow, and orange sulphides.—Mention the group-reagents usually employed in analysis.—Under what circumstances may a hydrochloric precipitate contain antimony or bismuth?—If a sulphuretted-hydrogen precipitate is white, what substances are indicated?—Give processes for the qualitative analysis of liquids containing the following substances:—*a.* Arsenium and Cadmium. *b.* Bismuth and Antimony. *c.* Ferrous and Ferric salts. *d.* Aluminium, Iron, and Chromium. *e.* Arsenium, Antimony, and Tin. *f.* Lead and Strontium. *g.* Iron, Sodium, and Arsenium. *h.* Mercury, Manganese, and Magnesium. *i.* Zinc, Manganese, Nickel, and Cobalt. *j.* Barium, Strontium, and Calcium.

THE ACIDULOUS RADICALS.

Introduction.—The twenty-seven radicals which have up to this point mainly occupied atttention are (admitting ammonium, NH_4) metals; and they have been almost exclusively studied not in the free state, but in the condition in which they exist in salts. Moreover, these metals have been treated as if they formed the more important constituent, the stronger part, the foundation or *base* of salts. Attention has been continuously directed to the metallic or *basylous* side of salts. And, indeed, there is still one more basylous radical which must be mentioned, though it is usually supposed to play only a subordinate part in medicine—Hydrogen. Unlike the salts of most metals, those of hydrogen (the so-called *acids*) are never, in medicine or the arts generally, professedly used for the sake of their hydrogen, but always for the other part of the salt, the *acidulous* side. And it is not for their basylous radical that these hydrogen salts are now commended to notice,* but in order to study, under the most favourable circumstances, those acidulous groupings which have continually presented themselves in operations on salts, but which were for the time of secondary importance. These *acidulous radicals* may now be treated as the primary object of attention; and there is no better way of doing so than by operating on their compounds with hydrogen, the relatively inferior medicinal importance of which element, as compared with potassium, iron, and other basylous radicals, will serve to give the desired prominence to the *acidulous radicals* in question.†

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* It must not be forgotten that the commonest salt of any radical whatsoever is a salt of hydrogen, the oxide of hydrogen (H_2O), or hydrate of hydrogen (HHO), *water*. In the reactions already performed, the value of this compound has been constantly recognised, both for its hydrogen and for its oxygen, but most of all as the vehicle or medium by which nearly all other atoms are enabled to come into that contact with each other without which their existence would be almost useless; for some atoms are like some animals—out of water they are as inactive as fishes. It is true that both fishes and salts have usually to be removed from water to be utilized by man; but before they can be assimilated, either as food or as medicine, they must again seek the agency of water—in becoming dissolved.

† Actually, it is as difficult to determine the relative importance of the different atoms or groups of atoms in a molecule as it is of the different parts or members of an animal or vegetable, the different units or societies in a community, the different planets or solar systems of the universe;

Common Acids.—These salts of hydrogen (hydrogen easily displaceable, wholly or, in certain cases, in part, by ordinary metals) are the common, sharp, sour bodies termed *acids* (from the Latin root *acies*, an edge). The following Table includes the formulæ and usual names of the most important: others will be noticed subsequently. A few of those mentioned are unstable or somewhat rare; in such cases a common metallic salt containing the acidulous radical may be used for reactions.

HCl	hydrochloric acid.	H_2S	sulphydric acid.†
HBr	hydrobromic acid.	H_2SO_3	sulphurous acid.
HI	hydriodic acid.	H_2SO_4	sulphuric acid.
HCN	hydrocyanic acid.	H_2CO_3 ?	carbonic acid.
HNO_3	nitric acid.	$H_2C_2O_4$	oxalic acid.
$HC_2H_3O_2$	acetic acid.*	$H_2C_4H_4O_6$	tartaric acid.

$H_3C_6H_5O_7$ citric acid. H_3PO_4 phosphoric acid. H_3BO_3 boric acid.

The usual names are here retained for these acids; but in studying their chemistry and chemical relations to other salts, they are usefully spoken of by such more purely chemical names as (for hydrochloric acid) chloride of hydrogen or hydrogen chloride, hydrogen nitrate, and so on—hydric or hydrogen sulphate, dihydric tartrate, trihydric phosphate, etc.

A prominent point of difference will at once be noticed between the basylous radicals met with up to the present time and the acidulous groupings included in the above tabular list. The former are nearly all elements, ammonium only being a compound; the latter are mostly compounds, chlorine, bromine, iodine, and sulphur being the only elements. This difference will not, however, be so apparent when the chemis-

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nay, the different pieces or parts of an engine or the different pigments or portions of a picture: *l'union fait la force.*

[*] The hydrogen on the acidulous side must not be confounded with the basylous hydrogen in all these hydrogen salts or acids; the two perform different functions. Hydrogen in the acidulous portion is like the hydrogen in the basylous radical ammonium; it has combined with other atoms, to form a group which plays more or less the part of an elementary radical. Cobalt, chromium, iron, platinum, etc., resemble hydrogen in this respect in often uniting with other atoms to form definite acidulous radicals in which the usual basylous character of the metals has for the time disappeared. In *hydrides* (p. 136) hydrogen itself is an acidulous radical.

[†] Synonyms: hydrosulphuric acid and sulphuretted hydrogen.

try of alcohols, ethers, and such bodies, has been mastered; for they may be regarded as salts of *compound* basylous radicals.

Rarer Acids.—The above acids contain the only acidulous groupings that commonly present themselves in analysis or in pharmaceutical operations. There are, however, several other acids (such as hypochlorous, nitrous, hypophosphorous, valerianic, benzoic, gallic, tannic, uric, hyposulphurous, hydroferrocyanic, hydroferricyanic, lactic, etc.) with which it is desirable to be more or less familiar; reactions concerning these will therefore be described. Arsenious, arsenic, stannic, manganic, and chromic acids have already been treated of in connexion with the metals they contain; in practical analysis these acids always become sufficiently altered for their metals to come out among the basylous radicals.

Quantivalence.—A glance at the foregoing table is sufficient to show the quantivalence of the acidulous radicals there mentioned. The first six are clearly univalent; then follow six bivalent, leaving three trivalent.

These all combine with equivalent amounts of basylous radicals to form various salts; hence they may be termed monobasylous, dibasylous, and tribasylous radicals. The acids themselves were formerly spoken of as monobasic, bibasic, and tribasic respectively, or monobasic and polybasic, in reference to the amount of *base* (hydrates or oxides) they could decompose; but the terms are no longer definite, and hence but little used in mineral chemistry.

Antidotes.—The antidotes in cases of poisoning by the strong acids will obviously be non-corrosive alkaline substances, as soap and water, magnesia, and common washing "soda" or other carbonates. Vinegar, lemon juice, and weak and non-corrosive acids would be the appropriate antidotes to caustic alkalies.

Analysis.—The practical study of the acidulous side of salts will occupy far less time than the basylous. Salts will then be briefly examined as a whole.

Caution.—Once more; it is only for convenience in the division of chemistry for systematic study that salts may be considered to contain basylous and acidulous radicals, or separate sides, so to speak; for we possess no absolute knowledge of the internal arrangement of the atoms (admitting that there are such things) in the molecule of the salt. We only know that certain groups of atoms may be transferred from compound to compound in mass (that is, without apparent decomposition); hence the assumption that these groups are radicals. A salt is probably a whole, having no such sides as those mentioned.

QUESTIONS AND EXERCISES.

Mention the basylous radical of acids.—Give illustrations of univalent, bivalent, and trivalent acidulous radicals, or monobasylous, dibasylous, and tribasylous radicals.—What is the difference between an elementary and a compound acidulous radical?—Name the grounds on which salts may be assumed to contain basylous and acidulous radicals.

HYDROCHLORIC ACID AND OTHER CHLORIDES.

Formula, HCl. Molecular weight,* 36·5.

The acidulous radical of hydrochloric acid and of other chlorides is the element chlorine (Cl). It occurs in nature chiefly as chloride of sodium (NaCl), either solid under the name *rock-salt*, mines of which are not uncommon, or in solution in the water of all seas. Common table-salt is more or less pure chloride of sodium in minute crystals. Chlorine, like hydrogen, is univalent (Cl'); its atomic weight is 35·5. Its molecule is symbolized thus, Cl_2.

Reactions.

Hydrochloric Acid.

First Synthetical Reaction.—To a few fragments of chloride of sodium in a test-tube or a small flask add about an equal weight of sulphuric acid; colourless and invisible gaseous hydrochloric acid is evolved, a sulphate of sodium remaining. Adapt to the mouth of the vessel, by a perforated cork, a piece of glass tubing bent to a right angle, heat the mixture, and convey the gas into a small bottle containing a little water; solution of hydrochloric acid results.

$$\underset{\text{Chloride of sodium.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Acid sulphate of sodium.}}{NaHSO_4}$$

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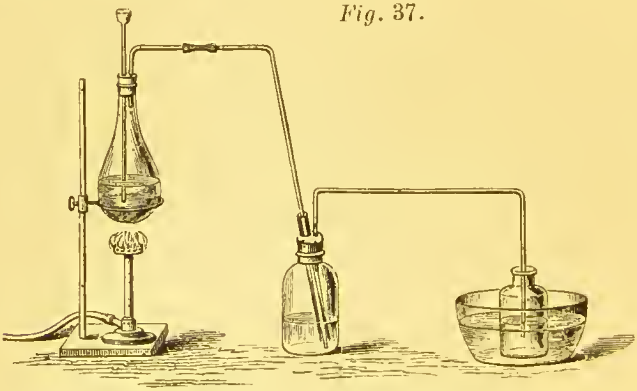
* The weight of a molecule is the sum of the weights of its atoms.

Hydrochloric acid.—The product of this operation is the nearly colourless and very sour liquid commonly termed hydrochloric acid. When of certain given strengths (estimated by volumetric analysis), it forms *Acidum Hydrochloricum*, B.P., and *Acidum Hydrochloricum Dilutum*, B.P. The former has a specific gravity of 1·16 (1·1578), and contains 31·8 per cent. of real acid; the latter, sp. gr. 1·052, with 10·58 per cent. of the real acid, is made by diluting 8 fluid parts of the strong acid with water until the mixture measures 26½ fluid parts. The above process is that of the Pharmacopœia—larger vessels being employed, and the gas being freed from any trace of sulphuric acid by washing. Other chlorides yield hydrochloric acid when heated with sulphuric acid; but chloride of sodium is always used because cheap and common.

Fig. 37.



PREPARATION OF HYDROCHLORIC ACID.

Common yellow hydrochloric acid is a by-product in the manufacture of carbonate of sodium from common salt by the process in which chloride of sodium is first converted into sulphate, hydrochloric acid being liberated. This impure acid is liable to contain iron, arsenium, fixed salts, sulphuric acid, sulphurous acid, nitrous compounds, and chlorine.

The official process for the preparation of hydrochloric acid is as follows: it may be carried out by the student with about one-twelfth of the quantities mentioned:—

"Take of chloride of sodium, dried, 48 ounces, sulphuric acid 44 fluid ounces, water 36 fluid ounces, distilled water 50 fluid ounces. Pour the sulphuric acid slowly into thirty-two ounces of the water, and, when the mixture has cooled, add it to the chloride of sodium previously introduced into a flask having the capacity of at least one gallon. Connect the flask by corks and a bent glass tube with a three-necked wash-bottle, furnished with a safety-tube, and containing the remaining four ounces of the water [or let the flask-tube pass loosely through a wider tube fixed in the cork of the wash-bottle, as shown in fig. 37]: then, applying heat to the flask, conduct the disengaged gas through the wash-bottle into a second bottle containing the distilled water, by means of a bent tube dipping about half an inch below the surface, and let the process be continued until the product measures sixty-six ounces, or the liquid has acquired a specific gravity of 1·16. The bottle containing the distilled water must be kept cool during the whole operation."

The modification of wash-bottle shown in the figure allows of the easy insertion or removal of a delivery-tube. The wider tube there shown, or an ordinary tube-funnel, also acts as a *safety-tube* by admitting the air the moment there is any tendency in the water in the receiver to be forced back on account of a too rapid absorption of the gas. The time of the student will be saved if hydrochloric acid already in stock be placed in the wash-bottle instead of water.

Invisible gaseous hydrochloric acid forms visible greyish-white fumes on coming into contact with air. This is due to combination with the moisture of the air. The intense greediness of hydrochloric gas and water for each other is strikingly demonstrated on opening a test-tube full of the gas under water; the latter rushes into and instantly fills the tube. If the water is tinged with blue litmus, the acid character of the gas is prettily shown at the same time. The test-tube, which should be perfectly dry, may be filled from the delivery-tube direct; for the gas is somewhat heavier than, and therefore readily displaces, air. The mouth may be closed by the thumb of the operator. At low temperatures hydrochloric acid and water form a crystalline compound, $HCl, 2H_2O$.

Note.—The process, as described in the British Pharmacopœia, includes the use of as much sulphuric acid as is necessary for the production of acid sulphate of sodium ($NaHSO_4$) which remains in the generating vessel. A hot solution of this residue, neutralized by carbonate of sodium, filtered and set aside, yields normal sulphate (*Sodii Sulphas*, B.P., the old Sulphate of Soda), in the form of transparent, oblique, efflorescent prisms ($Na_2SO_4, 10H_2O$).

$$\underset{\text{Acid sulphate of sodium.}}{2NaHSO_4} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Sulphate of sodium.}}{2Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Chlorine.

Second Synthetical Reaction.—To some drops of hydrochloric acid (that is, the common aqueous solution of the gas) add a few grains of black oxide of manganese, and warm the mixture; *chlorine*, the acidulous radical of all chlorides, is evolved, and may be recognised by its peculiar odour, or irritating effect on the nose and air-passages.

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2.$$

Chlorine-water.—This is the process of the British Pharmacopœia for the production of chlorine-water (*Liquor Chlori*, B.P.), the gas being first washed and then passed into water. One ounce of oxide to six fluid ounces of acid diluted with two of water, and the gas passed through a wash-bottle containing about two ounces of water, yield enough chlorine to produce about a pint and half of chlorine-water. (On this small scale, less than half the acid is utilized through incomplete decomposition of the materials and, especially, through incomplete absorption of the chlorine gas.) Chlorine slowly decomposes water with production of hydrochloric acid and oxygen gas; hence, for medicinal purposes, the solution should be freshly prepared; it is best preserved in a green-glass well-stoppered bottle in a cool and dark place. At common temperatures (60° F.), if fresh and thoroughly saturated, chlorine-water contains more than twice (2·3) its bulk of chlorine, or less than 1 per cent. (about 0·75) by weight. Chlorine passed into cold water yields crystals of hydrous chlorine ($Cl5H_2O$), and these, when heated under pressure, give an upper layer of chlorine-water and a lower layer of *liquid chlorine*.

Note.—To obtain the chlorine from other chlorides, sulphuric acid, as well as black oxide of manganese, must be added. Hydrochloric acid is first formed. The action described in the foregoing equation then goes on, except that half instead of the whole of the oxygen from the black oxide is employed for the removal of the hydrogen from the chlorine of the hydrochloric acid, the other half being taken up by the hydrogen of the sulphuric acid. Thus, assuming common salt to be the chloride used, the following equations may represent the supposed steps of the process :—

$$\begin{array}{lcccccccccc} & 2NaCl & + & H_2SO_4 & = & Na_2SO_4 & + & 2HCl, & & \\ & MnO_2 & + & H_2SO_4 & = & MnSO_4 & + & H_2O & + & O; \\ \text{then the} & 2HCl & + & O & = & H_2O & + & Cl_2; & & \end{array}$$

or the whole may be included in one equation.

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

This reaction may occasionally have analytical interest, a very small quantity of combined chlorine being recognised by its means. But the following test is nearly always applicable for the detection of this element, and leaves nothing to be desired in point of delicacy.

ANALYTICAL REACTIONS (TESTS).

To a drop of hydrochloric acid, or to a dilute solution of any other chloride, add solution of nitrate of silver; a white curdy precipitate (chloride of silver, $AgCl$) falls. Pour off the supernatant liquid, add nitric acid, and boil; the precipitate does not dissolve. Pour off the acid, and add dilute ammonia; the precipitate quickly dissolves. Neutralize the solution by an acid; the curdy precipitate again appears.

The formation of this white precipitate, its appearance, insolubility in boiling nitric acid, solubility in solution of ammonia or its carbonate, and reprecipitation by an acid, form abundant evidence of the presence of chlorine. Its occurrence as a chloride of a metal is determined by testing for the metal with the appropriate reagents; its occurrence as hydrochloric acid is considered to be indicated by the odour, if strong, and the sour taste, if weak, of the liquid, and the action of the liquid on blue litmus-paper, which, like other acids, it reddens. If hydrochloric acid be present in excessive quantity, it will, in addition to the above reactions, give rise to strong effervescence on the addition of a carbonate, a chloride being formed. The chlorine in insoluble chlorides, such as calomel, "white precipitate," etc., may be detected by boiling with alkali, filtering, acidulating the filtrate by nitric acid, and then adding the nitrate of silver.

Antidotes.—In cases of poisoning by strong hydrochloric acid, solution of carbonate of sodium (common washing-soda) or a mixture of magnesia and water, may be administered as an antidote.

QUESTIONS AND EXERCISES.

The official Hydrochloric Acid contains 31·8 per cent. by weight of gas, and its specific gravity is 1·16; work out a sum showing what volume of it will be required, theoretically, to mix with black oxide of manganese for the production of one gallon of chlorine-water, one fluid ounce of which contains 2·66 grains of chlorine. *Ans.*, 5½ fl. ozs. nearly (5·4).—Why does hydrochloric acid gas give visible fumes on coming into contact with air?—How much chloride of sodium will be required to furnish one pound of chlorine?—Give the analytical reactions of chlorides.—What antidotes may be administered in cases of poisoning by hydrochloric acid?

HYDROBROMIC ACID AND OTHER BROMIDES.

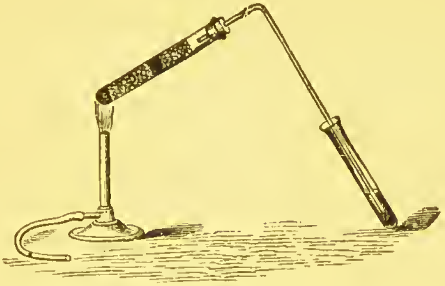
Formula of Hydrobromic Acid, HBr. Molecular weight, 81.

Bromine: Source, Preparation, and Properties.—The acidulous radical of hydrobromic acid and other bromides is the element bromine, Br (*Bromum*, B.P.). It occurs in nature chiefly as bromide of magnesium ($MgBr_2$) in sea-water and certain saline springs, and is commonly prepared from the *bittern*, or residual liquors of salt works. It may be liberated from its compounds by the process for chlorine from chlorides —that is, by heating with black oxide of manganese and sulphuric acid (*see* note on page 310). It is a dark-red volatile liquid, emitting an odour more irritating, if possible, than chlorine—of specific gravity 2·97 to 3·14; boiling point, 135–145° F.

Quantivalence.—The atom of bromine, like that of chlorine, is univalent (Br'). The atomic weight of bromine is 80. Free bromine has the molecular formula Br_2.

Hydrobromic Acid.—The bromide of hydrogen, hydrobromic acid, may be made by decomposing bromide of phosphorus by water—$PBr_5 + 4H_2O = 5HBr + H_3PO_4$. A small quantity is prepared by placing seven or eight drops of bromine at the bottom of a test-tube, putting in fragments of glass to the height of about an inch or two, then ten or eleven grains of phosphorus, then another inch of glass, and finally a couple of inches of glass fragments slightly wetted with water, a delivery-tube being fitted by a cork. The phosphorus combines readily, almost violently, with the bromine as soon as the vapour of the latter, aided by a little warmth from a flame, rises to the region of the phosphorus. The bromide of phosphorus thus formed then suffers decomposition by the water of the moist glass, phosphoric and phosphorous acids being produced. The hydrobromic acid gas passes over (heat being applied in the after part of the operation) and may be condensed in water or in solution of ammonia. The latter solution on evaporation yields bromide of ammonium.

Fig. 38.



PREPARATION OF HYDROBROMIC ACID.

Acidum Hydrobromicum Dilutum, B.P.—Pass sulphuretted hydrogen gas through bromine covered with water, and, when all bromine has disappeared, distil the mixture. The distillate, when diluted until it has a sp. gr. of 1·300, contains 33 per cent. of HBr. Diluted until the sp. gr. is 1·077, it contains 10 per cent. of HBr, and is then of official strength.

$$10\,Br_2 + 4H_2S + 8H_2O = 20HBr + 2H_2SO_4 + S_2.$$

Bromide of Potassium (KBr.) is very largely employed in pharmacy, and is the salt, therefore, which may be used in studying the reactions of this acidulous radical. The official method of making the salt has been alluded to under the salts of potassium (page 80).

Other bromides are seldom used; they may be prepared in the same way as, and closely resemble, the corresponding chlorides or iodides.

Bromide of Sodium crystallizes in anhydrous cubes ($NaBr$) from solutions at 110° F. or 120°, and in hydrous prisms ($NaBr, 2H_2O$) at ordinary temperatures.

Bromide of Ammonium (NH_4Br) (*Ammonii Bromidum*, B.P.) may be made by saturating hydrobromic acid with ammonia: $HBr + NH_4HO = NH_4Br + H_2O$. It forms colourless crystals which may become slightly yellow on exposure to air, is readily soluble in water, less so in spirit, and, when heated, sublimes.

Solution of Bromine, B.P., 10 minims in 5 ounces, is an aqueous solution, bromine being slightly soluble in water.

Hypobromites, *Bromates*, and *Perbromates*, analogous to hypochlorites, chlorates, and perchlorates, are producible.

Bromates, occurring as an impurity in bromides, are detected by dropping diluted sulphuric acid on to the salt, when a yellow colour due to free bromine is produced *immediately* if bromates are present.

Analytical Reactions (Tests).

First Analytical Reaction.—To a few drops of a solution of a bromide (KBr, or NH_4Br) add solution of nitrate of silver; a yellowish-white precipitate (bromide of silver, $AgBr$) falls. Treat the precipitate successively with nitric acid and dilute ammonia, as described for the chloride of silver; it is only sparingly dissolved in ammonia.

Second Analytical Reaction.—To solution of a bromide add a drop or two of chlorine water, or a bubble or two of chlorine gas; then add a few drops of chloroform or ether, or bisulphide of carbon, shake the mixture, and set the test-tube aside: the chlorine, from the greater strength of its affinities, displaces the bromine, which is dissolved by the chloroform, etc., the solution falling to the bottom of the tube in the case of the heavy chloroform or bisulphide of carbon, or rising to the top in the case of the light ether. Either solution has a distinct yellow, or reddish-yellow, or red colour, according to the amount of bromine present.

Notes.—This reaction serves for the isolation of bromine when mixed with many other substances. Excess of chlorine must be avoided, as colourless chloride of bromine is then formed. Iodides give a somewhat similar appearance; the absence of iodine must therefore be ensured by a process given in the next section. The above solution in chloroform or ether may be removed from the tube by drawing up into a *pipette* (small pipe—a narrow glass tube, usually having a bulb or expanded portion in the centre), the bromine fixed by the addition of a drop of solution of potash or soda, the chloroform or ether evaporated off, and the residue tested as described in the next reaction.

Third Analytical Reaction.—Liberate bromine from a bromide by the cautious addition of chlorine or chlorine-water, then add a few drops of cold "mucilage of starch" (*vide* Index); a yellow combination of bromine and starch, commonly termed "bromide of starch," is formed.

The above reaction may be varied by liberating the bromine by a little black oxide of manganese and a drop of sulphuric acid, the upper part of the inside of the test-tube being smeared over with the mucilage of starch. Even sulphuric acid alone, if strong, liberates bromine from a bromide, the hydrogen of the hydrobromic acid first produced uniting with the oxygen of the sulphuric acid—the latter being reduced to sulphurous acid or even to hydrosulphuric acid.

HYDRIODIC ACID AND OTHER IODIDES.

Formula of Hydriodic Acid, HI. Molecular weight, 128.

Source.—The acidulous radical of hydriodic acid and other iodides is the element iodine (I). It occurs in nature as iodides of sodium and magnesium, in sea-water. Sea-weeds, sponges, and other marine organisms, which derive much of their nourishment from sea-water, store up iodides in their tissues; and it is from the ashes of these that supplies of iodine (*Iodum*, B.P.) are obtained. Mineral iodides also are met with, and iodates occur in crude cubic nitre.

Process.—The sea-weed ash or *kelp* is treated with water, insoluble matter thrown away, and the decanted liquid evaporated and set aside to allow of the deposition of most of the sulphates, carbonates, and chlorides of sodium and potassium. The residual liquor is treated with excess of sulphuric acid, which causes evolution of carbonic and sulphurous or sulphuretted gases, deposition of sulphur and more sulphate of sodium, and formation of hydriodic acid. To the decanted liquid is added black oxide of manganese, and the mixture is then slowly distilled; the iodine sublimes and is afterwards purified by resublimation.

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2.$$

The analogy of chlorine, bromine, and iodine is well indicated by the fact that each is obtained from its compounds by the same reaction. Iodine is liberated from any iodide as bromine from bromides, or chlorine from chlorides—namely, by the action of black oxide of manganese and sulphuric acid.

Properties.—Iodine is a crystalline purplish-black substance; its vapour, readily seen on heating a fragment in a test-tube, is dark-violet. Its vapours are irritating to the lungs; but a trace may be inhaled with safety (*Vapor Iodi*, B.P.). It melts at 230° F., boils at about 392°, and is entirely volatilized, the first portions containing any cyanide of iodine that may be, though very rarely is, present. The latter body occurs in slender, colourless prisms, emitting a pungent odour.

Quantivalence.—The atom of iodine, like those of bromine and chlorine, is univalent[*] (I'). The atomic weight of iodine is 127; its molecular formula, I_2.

The Iodide of Hydrogen, or Hydriodic Acid, is a heavy, colourless gas. Its solution in water may be made by passing sulphuretted hydrogen into water in which iodine is suspended, the chief reaction being:—$2H_2S + 2I_2 = S_2 + 4HI$. See the analogous reaction for HBr, p. 313.

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[*] There is a compound of iodine having the formula ICl_3. Iodine would at first sight therefore seem to be a trivalent element (I'''); and bromine and fluorine, from their close chemical analogy with iodine, would necessarily be regarded as trivalent also. From this aspect the position of chlorine would be anomalous. Probably, however, the compound is only a molecular combination of true chloride of iodine, ICl, with added chlorine, Cl_2. Iodine forms, with iodide of potassium, a periodide or tri-iodide, KI_3, which may be obtained in lustrous prismatic crystals. This, too, may have the formula KI, I_2. A mercuric hexiodide (HgI_6, perhaps HgI_2, I_2, I_2) is also known; and a periodide of ammonium, NH_4I, I_2: both, probably, only "additive" compounds. See p. 155.

Hydriodic acid may also be prepared by placing twenty parts of iodine and two of water in a retort the neck of which points upwards, and the end of the neck of which is connected by a glass tube with a bottle or other vessel containing a little water. Into the tubulure of the retort is passed, at first a drop at a time, a mixture of one part of red phosphorus with two of water. Abundance of hydriodic acid is evolved on the application of a gentle heat, and falls into and dissolves in the water in the receiver. Phosphoric acid remains.—$P_2 + 5I_2 + 8H_2O = 10HI + 2H_3PO_4$. See the analogous reaction for HBr, p. 312.

Or iodine may be dissolved in bisulphide of carbon in a tall cylinder, water added, and sulphuretted hydrogen passed through the mixture. The water dissolves the hydriodic acid produced, the bisulphide retaining the separated sulphur. The aqueous solution only needs boiling for two or three minutes to remove excess of sulphuretted hydrogen.

Iodide of potassium (KI) is largely used in medicine, and hence is the most convenient iodide on which to experiment in studying the reactions of this acidulous radical. Solid iodine itself might be taken for the purpose; but its use and action in that state having already been alluded to in describing the iodides of potassium, cadmium, and mercury, its analytical reactions in the combined condition are those which may now occupy attention.

Solution of Iodine. Iodine is slightly soluble in water (iodine-water), and readily soluble in an aqueous solution of iodide of potassium. Ten grains of iodine and fifteen of iodide of potassium, dissolved in sufficient distilled water to produce 200 fluid grains, forms *Liquor Iodi*, B.P. (*see* footnote on previous page); 32 grains of iodine and 32 of iodide of potassium, rubbed with 1 fluid drachm of glycerine, and 2 ounces of lard gradually mixed in, form *Unguentum Iodi*, B.P. It is more soluble in spirit, or in a spirituous solution of iodide of potassium (*Tinctura Iodi*, B.P.). It combines with sulphur, forming an unstable, greyish-black, solid iodide (S_2I_2), having a radiated crystalline structure (*Sulphuris Iodidum*, B.P., and *Unguentum Sulphuris Iodidi*). "If 100 grains be thoroughly boiled with water, the iodine will pass off in vapour, and about 20 grains of sulphur remain."—*Brit. Pharm.*

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To a few drops of an aqueous solution of an iodide (*e.g.* KI) add solution of nitrate of silver; a light yellow precipitate (iodide of silver, AgI) falls. Pour away the supernatant liquid, and treat the precipitate with nitric acid; it is not dissolved. Pour away the acid, and then add dilute ammonia; it is only sparingly dissolved.

This reaction is useful in separating iodine from most other acidulous radicals, but does not distinguish iodine from bromine.

The presence of chloride in iodide of silver may be detected by boiling with dilute solution of carbonate of ammonium, filtering off the insoluble iodide of silver, and saturating the filtrate with nitric acid; any chloride of silver is then precipitated.

Ammonia, it will be remembered, dissolves chloride of silver readily; hence the presence of chloride of potassium in bromide or iodide may be detected by dissolving in water, adding excess of nitrate of silver, collecting the precipitate, washing, digesting in ammonia, filtering, and adding excess of nitric acid to the filtrate; more than a trace of white curdy precipitate indicates a chloride (of potassium). Bromide and iodide of silver are, however, slightly soluble in ammonia. Better processes are given on pages 320 to 323.

Second Analytical Reaction.—Liberate iodine from an iodide by the cautious addition of chlorine, then add mucilage of starch; a deep-blue combination of iodine and starch, commonly termed "iodide of starch," is formed.

Starch is highly sensitive to the action of iodine; this reaction is consequently very delicate and characteristic. Heat decomposes the blue compound. Excess of chlorine must be avoided, or colourless chloride of iodine will be produced. Nitrous acid, or a nitrite acidulated with sulphuric acid, may be used instead of chlorine. Concentrated sulphuric acid also liberates iodine from iodides, the hydrogen of the hydriodic acid first produced uniting with the oxygen of the sulphuric acid—the latter (H_2SO_4) being reduced to sulphurous acid (H_2SO_3), or even to hydrosulphuric acid (H_2S).

In testing bromine for iodine, the bromine must be nearly all converted into hydrobromic acid by dilute solution of sulphurous acid, or be nearly all removed by solution of soda, before the mucilage of starch is added.

Ozone (O_3).—Papers soaked in mucilage of starch containing iodide of potassium form a test for free chlorine and nitrous acid, and are also employed by meteorologists to detect an allotropic or physically polymeric and energetic form of oxygen, termed by Schönbein *ozone* (from ὄζω, *ozō*, I smell). This substance liberates iodine from the iodide of potassium (with formation of iodide of starch), and is supposed to occur normally in the atmosphere, the salubrity or insalubrity of which is said to be dependent to some extent on the presence or absence of ozone. The possible occurrence of nitrous or chlorinoid gases in the air, however, renders the test untrustworthy. Houzeau proposes to test for ozone by exposing litmus-paper of a neutral tint soaked in a dilute solution of iodide of potassium : the potash set free by action of the ozone turns the paper blue. The same paper without iodide would indicate the extent to which the effect might be due to ammonia vapour. Ozone, or, rather, ozonized air, is produced artificially in large quantities on passing air through a box (Beane's Ozone-generator) highly charged with electricity. In the latter operation condensation of the volume of air, or, rather, of the oxygen in the air, occurs. Small quantities are obtained by exposing in a loosely closed bottle a stick of phosphorus partially covered by water, but the product is mixed with peroxide of hydrogen. Ozone is a powerful bleaching, disinfecting, and general oxidizing agent; insoluble in water, soluble in oils of turpentine, cinnamon, and some other liquids. From experiments that have been made by Soret on the specific gravity of ozone, its molecular formula would seem to be O_3, that of ordinary oxygen being O_2. Its smell is peculiar.

Third Analytical Reaction.—To a neutral aqueous solution of an iodide add a solution containing one part of sulphate of copper to two and a half parts of green sulphate of iron, and well shake; a dirty-white precipitate of cuprous iodide (Cu_2I_2) falls.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_23SO_4.$$

Or to the liquid containing an iodide add the solution of copper sulphate and some solution of sulphurous acid, and warm the mixture; cuprous iodide falls.

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4.$$

Separation of Chlorides, Bromides, and Iodides.—Chlorides and bromides are not affected in the above way; the reaction is useful, therefore, in removing iodine from a solution in which chlorides and bromides have to be sought. The total removal of iodine by the former of the two modifications of the process is ensured by supplementing the addition of the cupric and ferrous sulphates by a few drops of solution of potash or soda, any acid which might be keeping cuprous iodide in solution being thereby neutralized, ferric or ferrous hydrate, precipitated at the same time, not affecting the reaction. Occasionally, too, it may be necessary to repeat the process with the filtrate before the last traces of iodine are removed. The second modification of the process is, on the whole, to be preferred.

Chlorides may be separated from bromides by taking advantage of the ready solubility of chloride of silver, and the slow and slight solubility of bromide of silver, in ammonia, especially in (a fair, not a great, excess of) ammonia containing chloride of silver. The presence of much bromide of silver, however, considerably reduces the power of ammonia to dissolve chloride of silver.

Hart's Test.—(If nitrates, chlorates, bromates, or iodates are present, it is necessary to fuse the substance with a little sodium carbonate and charcoal to reduce them. If the haloids are united with silver, it is best to fuse with sodium carbonate and extract with water, although with iodine and bromine this is not absolutely necessary.) The substance is placed in the flask shown in the figure given in the section on the quantitative analysis of oxide of manganese (*vide* Index), with some water and a few drops of solution of ferric sulphate. Into the bulbs are poured a few drops of dilute starch-mucilage. The bulbs are kept cold by immersing in water in a beaker. The contents of the flask are then boiled, and if iodine is present the starch is coloured blue. This test is extremely delicate. If iodine is found, the cork with the bulb tube is removed, and the solution boiled until, on testing again in the same way, no more iodine is found. If much iodine is present, it is necessary to add more ferric sulphate solution. The bulb tube is now cleaned, charged with a few drops of water and a drop or two of chloroform, and a very small crystal of potassium permanganate added to the solution in the flask. The contents of the flask are boiled again, and if bromine is present the chloroform becomes red. The tube is now removed, and more permanganate of potassium and ferric sulphate added little by little, the mixture being boiled between each addition until the bromine has all been driven off. A few drops of alcohol are added to the contents of the flask, to decolorize any excess of permanganate, and after filtration chlorine is tested for in the filtrate with silver nitrate.

Chlorides may also be detected in bromides and iodides by taking advantage of the formation of chlorochromic anhydride (page 275) and the non-occurrence of corresponding compounds of bromine or iodine, as follows :—

To a solution of a mixture of an iodide with a bromide and a chloride add a concentrated solution of sulphite of sodium, then a reagent prepared by mixing equal volumes of sulphuric acid and saturated solution of sulphate of copper, until no further precipitation of cuprous iodide occurs. Next add solution of soda to remove excess of sulphate of copper, filter, and evaporate to dryness. Transfer the dried residue, together with an equal bulk of red chromate of potassium, to a dry test-tube fitted with a delivery-tube, or to a small retort, and cover the mixture with sulphuric acid. Distil into water. Chromic anhydride and hydrochloric and hydrobromic acids are liberated by the sulphuric acid, and, reacting one upon another, form chlorochromic anhydride, together with free bromine and chlorine.

$$\begin{aligned} CrO_3 + 2HCl &= CrCl_2O_2 + H_2O \\ 2CrO_3 + 6HBr + 3H_2SO_4 &= Cr_2 3SO_4 + 3Br_2 + 6H_2O \\ 2CrO_3 + 6HCl + 3H_2SO_4 &= Cr_2 3SO_4 + 3Cl_2 + 6H_2O. \end{aligned}$$

The chlorochromic anhydride is decomposed by the excess of water into which it distils, giving rise to chromic acid, which imparts its colour to the liquid, and hydrochloric acid, thus :

$$CrCl_2O_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Chlorine gas escapes and the bromine is dissolved by the water. The coloured liquid is then shaken with chloroform, which removes the bromine, indicating bromides in the original substance. A yellow colour remaining is due to chromic acid, indicating chlorides in the original substance. Or add ammonia to the distillate—the colour due to bromine is thereby entirely removed, while that of the chromic compound is only slightly modified.

Instead of eliminating the iodine as cuprous iodide, it may be expelled in vapour, obvious enough by its colour and odour, by fusing the dry mixture of the salts with excess of powdered red chromate. The residue, broken into small fragments, may then be distilled with the sulphuric acid for the detection of the bromine and chlorine.

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 3I_2$$

Fourth Analytical Reaction.—Iodides have been shown to be useful in testing for mercuric salts (*see* the Mercury Reactions, page 235); a mercuric salt (corrosive sublimate, for example) may therefore be used in testing for iodides, a scarlet precipitate (mercuric iodide, HgI_2) being produced.

This reaction may be employed where large quantities of an iodide are present; but its usefulness in analysis is much impaired by the fact that the precipitate is soluble in excess of the dissolved iodide, or in excess of the mercuric reagent. Its colour and insolubility in water distinguish it from mercuric chloride, bromide, and cyanide, which are white soluble salts.

Fifth Analytical Reaction.—Iodides have also (*see* the Lead Reactions, page 246) been shown to be useful in testing for lead salts; similarly a lead salt (acetate, for example) may be used in testing for iodides, in solutions which are either neutral or faintly acid with acetic acid, a yellow precipitate (iodide of lead, PbI_2), soluble in hot water and crystallizing in yellow scales on cooling, being produced.

Chloride, bromide, and cyanide of lead are white; hence the above reaction may occasionally be useful in distinguishing iodine from the allied radicals. But iodide of lead is slightly soluble in cold water; hence small quantities of iodine cannot be detected by this reaction. (For Iodates, *see* Index.)

Analogies between Chlorine, Bromine, Iodine and their Compounds.—These elements form a natural group or family, each distinct from the other, yet closely related. Moreover, their dissimilarities are so curiously gradational as to irresistibly suggest the idea that some day we may find the differences between these bodies to be in degree rather than in kind. Thus chlorine is a gas and iodine a solid, while bromine occupies the intermediate condition. The atomic weight of bromine is nearly midway between those of chlorine and iodine. The same may be said of the weight of equal volumes of each in the gaseous state. The specific gravity of fluid chlorine is 1·33, of iodine 4·95, while bromine is nearly 3. Liquid chlorine is transparent, iodine opaque, bromine intermediate. The crystalline forms of the chloride, bromide, and iodide of a metal are commonly identical. One volume of either element in the gaseous state combines with an equal volume of hydrogen (at the same temperature) to form two volumes of a gaseous acid, very soluble in water (hydrochloric acid, hydrobromic acid, hydriodic acid). Many other analogies are traceable. (*Vide* Index, "Periodic Law.")

QUESTIONS AND EXERCISES.

State the method by which bromine is obtained from its natural compounds.—Mention the properties of bromine.—How may the bromides of potassium and ammonium be made?—By what reagents may bromides be distinguished from chlorides?—Whence is iodine obtained?—By what process is iodine isolated?—State the properties of iodine.—What is the nature of iodide of sulphur?—Give the analytical reactions of iodides.—What three substances may, indirectly, be detected by a mixture of iodide of potassium and mucilage of starch?—Describe a method by which iodides may be removed from a solution containing chlorides and bromides.

HYDROCYANIC ACID AND OTHER CYANIDES.

Formula of Hydrocyanic Acid, HCN or HCy.
Molecular weight, 27.

History of Cyanogen.—The acidulous radical of hydrocyanic acid and other cyanides is a compound body, cyanogen (CN or, shortly, Cy or C_2N_2 or $N{\equiv}C{-}C{\equiv}N$). It is so named from κύανος, *kuanos*, blue, and γεννάω, *gennao*, I generate, in allusion to its prominent chemical character of forming, with iron, the different varieties of Prussian blue. It was from Prussian blue that Scheele in 1782 first obtained what we now, from our knowledge of its composition, term hydrocyanic acid (HCy, or HCN, or $H{-}C{\equiv}N$), but which he called Prussic acid. Cyanogen was isolated by Gay-Lussac in 1814, and was the first compound radical distinctly proved to exist.

Sources.—Cyanogen does not occur in nature, and is only formed from its elements under certain circumstances. It is found in small quantities among the gases of iron furnaces, and is produced to a slight extent in distilling coals for gas. In the form of ferrocyanide of potassium it is obtained abundantly by heating animal refuse containing nitrogen, such as the scrapings of horns, hoofs, and hides (5 parts), with carbonate of potassium (2 parts) and waste iron (filings, etc.) in a covered iron pot. The residual mass is boiled with water, the mixture filtered, and the filtrate evaporated and set aside for crystals to form. The cyanogen, produced from the carbon and nitrogen of the animal matter, unites with the potassium and afterwards, on boiling with water, with iron, to form what is often termed the yellow prussiate of potash, or ferrocyanide of potassium, *Potassii Ferrocyanidum*, B.P. ($K'_4Fe''Cy'_6$, $3H_2O$), a compound occurring in four-sided tabular yellow crystals. It contains the elements of cyanogen, yet is not a cyanide, for it is not poisonous, and is otherwise different from cyanides: it will be further noticed subsequently. From this salt all cyanides are directly or indirectly prepared.

Cyanide of potassium (KCy), the most common cyanide, may be obtained by heating the ferrocyanide to redness until gas (chiefly nitrogen) ceases to be evolved; and carbide of iron settles to the bottom of the molten mass of almost pure cyanide (*Potassii Cyanidum*, B.P.). The product, carefully poured off and cooled, is an opaque crystalline mass containing about 95 per cent. of the salt. It also may be procured by fusing eight parts of ferrocyanide of potassium with three of carbonate of potassium in a crucible; carbonic acid gas (CO_2) is evolved, iron (Fe) is set free, and cyanate of potassium (KCyO), a body that will be subsequently noticed, is formed at the same time:—

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KCyO + Fe_2 + 2CO_2.$$

Double cyanides exist, such as the cyanide of sodium and silver (NaCy, AgCy) formed in the process (subsequently described) of quantitatively determining the amount of hydrocyanic acid in a liquid by a standard solution of nitrate of silver: these compounds have, more or less, the properties of their constituents. But other cyanogen compounds, not double cyanides, occur, in which the cyanogen is so intimately united with a metal as to form a distinct radical: such are ferrocyanides and ferricyanides—salts which will be noticed in due course.

Cyanogen, like chlorine, bromine, and iodine, is univalent (Cy'). It may be isolated by simply heating mercuric cyanide ($HgCy_2$) or cyanide of silver (AgCy). It is a colourless gas, burning, when ignited, with a beautiful peachblossom-coloured flame.

Mercuric cyanide is produced in crystals on dissolving 1 part of ferrocyanide of potassium in 15 parts of boiling water, adding 2 parts of mercuric sulphate, keeping the whole hot for ten or fifteen minutes, and then filtering and setting aside to cool. In addition to mercuric cyanide ($HgCy_2$), mercury (Hg), ferric sulphate (Fe_23SO_4), and sulphate of potassium (K_2SO_4), are formed. Any excess of ferrocyanide also gives Prussian blue by reaction with the ferric sulphate. A small flame of cyanogen may be obtained on heating a few crystals of mercuric cyanide in a short piece of glass tubing closed at one ond, and applying a light to the other end as soon as evolution of gas commences: brown *paracyanogen* (C_3N_3) and mercury remain.

REACTIONS.

Diluted Hydrocyanic Acid.

Synthetical Reaction.—Dissolvo 2 or 3 grains of ferrocyanide of potassium in 5 or 6 times its woight of water in a test-tube, add a few drops of sulphuric acid and boil the mixture, conveying the evolved gas by a bent glass tube (adapted to the test-tube by a cork) into another test-tube containing a little water; the product is a dilute solution of hydrocyanic acid. Made by this process in larger quantities and of a certain definite strength (2 per cent.), this solution is the *Acidum Hydrocyanicum Dilutum*, B.P. "A colourless liquid of peculiar odour. Specific gravity, 0·997."

$$2K_4FeCy_6 + 6H_2SO_4 = Fe''K_2FeCy_6 + 6KHSO_4 + 6HCy.$$

The details of the official process are as follows:—Dissolve $2\frac{1}{4}$ ounces of ferrocyanide of potassium in 10 ounces of water, add one fluid ounce of sulphuric acid previously diluted with 4 ounces of water and cooled. Put the solution into a flask or other suitable apparatus of glass or earthenware, to which are attached a condenser and a receiver arranged for distillation (*see* p. 141); and having put 8 ounces of distilled water into the receiver, and provided efficient means for keeping the condenser and receiver cold, apply heat to the flask, until by slow distillation the liquid in the receiver is increased to 17 fluid ounces.* Add to this 3 ounces of distilled water, or as much as may be sufficient to bring the acid to the required strength, so that 100 grains (or 110 minims) of it, precipitated with a solution of nitrate of silver (*vide* paragraphs on quantitative analysis), shall yield 10 grains of dry cyanide of silver. The end of the condenser or an attached tube should pass quite into the receiver.

The residue of this reaction is acid sulphate of potassium ($KHSO_4$), which remains in solution, and ferrocyanide of potassium and iron ($Fe''K_2FeCy_6$), an insoluble powder sometimes termed Everitt's yellow salt, from the name of the chemist who first made out the nature of the reaction. The latter compound becomes bluish green during the reaction, owing to the absorption of oxygen.

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* This operation is peculiarly liable to those sudden and tumultuous evolutions of vapour, or "bumpings," or "*soubresauts*," which often interfere with successful distillation. Such phenomena occur, according to Tomlinson, whenever unaided heat has to overcome the great amount of adhesion naturally existing between certain liquids and vapours, or, rather, between the normal liquid and those particles of it which, becoming strongly heated at the heated part of the vessel, have assumed the condition of particles of dissolved vapour, and which would at once pass from this condition into that of permanent vapour but for adhesion. Ordinarily a glass or other surface is not absolutely clean, but is more or less covered with specks, traces of materials deposited from the air, the fingers, cloths, etc. Some liquids seem to have little or no adhesion for these materials, while certain vapours have greater adhesion for the films than for the liquids. Hence, in ordinary regular ebullition the vapours

Pure anhydrous hydrocyanic acid is a colourless, highly volatile, intensely poisonous liquid, solidifying when cooled to a low temperature.* It may be made by passing sulphuretted hydrogen over mercuric cyanide. The official solution of the acid is fairly stable, but is said to be rendered more so by the presence of a minute trace of sulphuric or hydrochloric acid. A stronger acid is liable to assimilate the elements of water, and yield formate of ammonium (NH_4CHO_2). Solutions of hydrocyanic acid often become brown by formation of what is, apparently, *paracyanogen* (C_3N_3). According to Williams, aqueous hydrocyanic acid containing 20 per cent. of glycerine can be kept for an almost indefinite length of time. The official acid should be preserved in well-corked bottles tied over with impervious tissue and kept inverted, when not in use, in a cool, dark place. Unless such precautions are adopted, the fluid rapidly loses strength by escape of the vapour of the acid.

Note.—A few drops of diluted hydrocyanic acid so placed that its vapour may be inhaled, forms the *Vapor Acidi Hydrocyanici*, B.P., or Inhalation of Hydrocyanic Acid.

Hydrocyanic acid also occurs in cherry-laurel water and

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accumulate on the films, and then at once become subject to the pressure of the mass of fluid, and so pass off in bubbles. But when the films are absent, or have become removed during distillation, the heat accumulates until it is sufficient to overcome the adhesion of the superheated particles, and these are then, all of them at once, converted into vapour, the liquid sometimes boiling over, or even bursting the vessel. "Bumping" may be prevented by using glass vessels roughened inside (by hydrofluoric acid or otherwise) or by inserting fragments of substances for which vapour-particles have adhesion, but no known substance has this property in an absolute degree. Tobacco-pipe or pumice-stone, pieces of cork, thick paper, resin, sulphur, platinum wire, etc., are useful when there is no chemical action between them and the liquid. Tomlinson recommends cocoanut-shell charcoal. A slow current of gas, such as hydrogen, air, or carbonic acid gas, also promotes escape of vapour from a liquid; a few capillary tubes, sealed at one end, and placed mouth downwards in the fluid, answering well. A jet of steam prevents bumping, but is not always applicable.

* Traces are formed when electricity passes between carbon poles in slightly moist air (Dewar).

bitter-almond water (*vide* Index). *Aqua Laurocerasi*, B.P., is made to contain 0·1 per cent. of real acid (HCy).

The methods of determining the strength of hydrocyanic acid solutions will be given in connection with volumetric and gravimetric quantitative analysis. They are based on the formation of cyanide of silver, and its solubility in solution of alkaline cyanides, as described in the next reaction.

The Hydrocyanic Acid used in pharmacy is extremely liable to variation in strength. It should frequently be tested volumetrically.

Analytical Reactions (Tests).

First Analytical Reaction.—To a few drops of the hydrocyanic acid solution produced in the above reaction, or to any solution of a cyanide, add excess of solution of nitrate of silver; a white precipitate (cyanide of silver, AgCy) falls. When the precipitate has subsided, pour away the supernatant liquid and place half of the residue in another test-tube: to one portion add nitric acid, and notice that the precipitate does not dissolve; to the other add ammonia, and observe that the precipitate, though soluble, dissolves somewhat slowly. (Chloride of silver, which is also white, is readily soluble in ammonia.) Cyanide of silver dissolves in solution of cyanides of alkali-metals, soluble double cyanides being formed (*e.g.*, KCyAgCy).

Solubility of precipitates in strong solutions of salts.—Cyanide of silver and many other precipitates insoluble in acids (similar remarks apply to precipitates insoluble in alkalies) are often soluble in the saline liquids formed by the addition of acids and alkalies to each other. Hence the precaution of adding the latter reagents to separate portions of a precipitate, or of not adding the one until the other has been poured away.

Cyanogen in an insoluble cyanide, such as cyanide of silver itself, is readily recognised on heating the substance in a short piece of glass tubing closed at one end like a test-tube and drawn out at the other end, so as to have but a small opening; on applying a flame, the escaping cyanogen ignites and burns with a characteristic peach-blossom tint. Metallic silver remains.

Antidote.

Second Analytical Reaction.—To a dilute solution of hydrocyanic acid, or a soluble cyanide, add a few drops of solution of a ferrous salt and a drop or two of solution of a ferric salt (ferrous sulphate and ferric chloride are usually at hand); to the mixture add potash, soda, magnesia, or carbonate of sodium, and then hydrochloric acid; a precipitate of Prussian blue remains. The decompositions may be traced in the following equations :—

$$\begin{array}{lclclcl} HCy & + & KHO & = & KCy & + & H_2O \\ 2KCy & + & FeSO_4 & = & FeCy_2 & + & K_2SO_4 \\ 4KCy & + & FeCy_2 & = & K_4FeCy_6 \text{ or } K_4Fcy \\ 3K_4Fcy & + & 2Fe_2Cl_6 & = & 12KCl & + & Fe_4Fcy_3. \end{array}$$

The test depends on the conversion of the cyanogen into ferrocyanogen by aid of the iron of a ferrous salt, and the combination of the ferrocyanogen, so produced, with the iron of a ferric salt.

Hence a mixture of green sulphate of iron, solution of perchloride of iron, and either magnesia or carbonate of sodium is the recognised *antidote* in cases of poisoning by hydrocyanic acid or cyanide of potassium.

In such an alkaline mixture the poisonous cyanide, by reaction with ferrous hydrate, is at once converted into innocuous ferrocyanide of potassium or sodium, etc.: should the mixture become acid, the ferric salt present reacts with the soluble ferrocyanide, forming insoluble Prussian blue, which is also inert. From the rapidity of the action of these poisons, however, there is seldom time to prepare an antidote. Emetics, the stomach-pump, or stomach-siphon, the application of a stream of cold water to the spine, and the above antidote, form the usual treatment.

Third Analytical Reaction.—To solution of hydrocyanic acid add ammonia and common yellow sulphydrate of ammonium, and evaporate the liquid nearly or quite to dryness in a small dish, occasionally adding ammonia till the excess of sulphydrate of ammonium is decomposed; add water and acidify the liquid with hydrochloric acid, and then add a drop of solution of a ferric salt; a blood-red solution of sulphocyanate of iron will be formed.

This is a very delicate reaction. Some free sulphur in the yellow sulphydrate of ammonium unites with the alkaline cyanide and forms sulphocyanate ($2NH_4Cy + S_2 = 2NH_4CyS$); the ammonia combines with excess of free sulphur and forms, among other salts, sulphydrate of ammonium, the whole of which is removed by the ebullition. If the liquid has not been evaporated far enough, sulphydrate of ammonium may still be present, and give black sulphide of iron on the addition of the ferric salt, hence prior acidification.

Hydrocyanic acid in the blood.—According to Buchner, the blood of animals poisoned by hydrocyanic acid, instead of coagulating as usual, remains liquid, and of a clear cherry-red colour for several days. In one case he obtained the reactions of the acid on diluting and distilling the blood fifteen days after death, and applying the usual reagents to the distillate. Aqueous solution of peroxide of hydrogen changes such blood to a deep-brown colour.

Schonbein's test for hydrocyanic acid is said to be extremely delicate. Filtering-paper is soaked in a solution of 3 parts of guaiacum resin in 100 of alcohol. A strip of this paper is dipped in a solution of 1 part of sulphate of copper in 50 of water; a little of the suspected solution is placed on this paper and exposed to the air, when it immediately turns blue. Or the paper may be placed over the neck of an open bottle of medicine supposed to contain hydrocyanic acid, or otherwise exposed to the suspected vapour of the acid.

QUESTIONS AND EXERCISES.

Write a paragraph on the history of cyanogen.—Mention the source of the cyanogen of cyanides.—How is Ferrocyanide of Potassium prepared?—What is the formula of ferrocyanide of potassium?—Is ferrocyanide of potassium poisonous?—Write an equation expressive of the reaction which ensues when ferrocyanide and carbonate of potassium are brought together at a high temperature.—What are the properties of cyanogen? How may it be obtained in a pure condition?—How is mercuric cyanide prepared? What other substances and secondary products are formed at the same time?—How much real hydrocyanic acid is contained in the official *Acidum Hydrocyanicum Dilutum*?—Give details of the preparation of hydrocyanic acid, and an equation of the reaction.—State the proportion of water that must be added to an aqueous solution containing

15 per cent. of hydrocyanic acid to reduce the strength to 2 per cent. *Ans.*, 6½ to 1.—What are the characters of pure undiluted hydrocyanic acid? How may it be obtained?—Enumerate the tests for cyanogen, giving equations.—Explain the action of the best antidote in cases of poisoning by hydrocyanic acid or cyanide of potassium. Show how it acts in alkaline and acid solutions respectively.

NITRIC ACID AND OTHER NITRATES.

Formula of the Acid, HNO_3 or $HONO_2$. Molecular weight, 63.

Introduction.—The group of elements represented by the formula NO_3 is that characteristic of nitric acid and all other nitrates; hence it is expedient to regard these elements as forming an acidulous radical, which may be termed *the nitric radical.* Like the hypothetical basylous radical ammonium, (NH_4), this supposed acidulous radical (NO_3) has not been isolated. Possibly it is liberated when chlorine is brought into contact with nitrate of silver; but if so, its decomposition into white crystalline nitric anhydride (N_2O_5) and oxygen (O) is too rapid to admit of its identification.

Sources.—The nitrogen and oxygen of the air combine and ultimately form nitric acid whenever a current of electricity (as in the occurrence of lightning) passes. The nitrates found in rain may partly or wholly thus originate. The oxidation of ammoniacal matter, and of the nitrogenous constituents of animal and vegetable matters in the soil, favoured by the darkness, by the occurrence of carbonate of calcium, and by the presence of some low form of vegetable life acting as a ferment, result in the production of nitrates. Hence nitrates are commonly met with in waters, soils, and the juices of plants. In the concentrated plant juices, termed medicinal "Extracts," small prismatic crystals of nitrate of potassium may occasionally be observed. (The cubical crystals often met with in extracts are chloride of potassium.) Nitric acid and other nitrates are obtained from nitrates of potassium and sodium, and these from the surface layers of the soil of tropical countries. *Nitrate of potassium*, or *prismatic nitre* (from the form of its crystals), is chiefly produced in and about the villages of India. The natives simply scrape the surface of waste grounds, mud-heaps, banks, and other spots where a slight incrustation indicates the presence of appreciable quantities of nitre, mix the scrapings with wood-ashes (carbonate of potassium, to decompose the nitrate of calcium always present), digest the mixture in water, and evaporate the liquor. The immediate product is purified by careful recrystallizations, and is sent into commerce in the form of white crystalline masses or fragments of striated six-sided prisms. Besides its use in medicine (*Potassii Nitras*, B.P.), it is employed in very large quantities in the manufacture of gunpowder. *Nitrate of sodium* (*Sodii Nitras*, B.P.), the old Nitrate of Soda, occurs in deposits from 3 inches to 3 yards in thickness on and near the surface, and at any depth down to about 30 feet, in many parts of Peru, Bolivia, and Chili, but more especially in the district of Atacama. The mineral is termed *caliche*, and commonly contains 50 per cent. of nitrate of sodium. The latter is distinguished as *Chili saltpetre* or *Chili nitre*, or (from the form of its crystals—obtuse rhomboids, not true cubes) *cubic nitre*, and is chiefly used as a manure and as a source of nitric acid, its tendency to absorb moisture unfitting it for use in gunpowder. In many parts of Europe nitrate of potassium is made artificially by exposing heaps of animal manure, refuse, ashes, and soil to the action of the air and the heat of the sun; in the course of a year or two the nitrogen of the animal matter becomes oxidized to nitrates; the latter are removed by washing. According to Warington, the nitrifying ferment appears capable of existing in three conditions: (1) The nitric ferment of soil, which converts both ammonium salts and nitrites into nitrates; (2) the altered ferment, which converts ammonium salts into nitrites, but fails to change nitrites into nitrates; and (3) the surface organism (a bacterium), which changes nitrites into nitrates. Similar nitrification goes on in impure well and river waters, which thereby tend to become pure.

Note.—The word *nitric* is from *nitre*, the English equivalent of the Greek *νίτρον* (*nitron*), a name applied to certain natural deposits of *natron* (carbonate of sodium), for which nitrate of potassium seems at first to have been mistaken. *Saltpetre* is simply *sal petræ*, salt of the rock, in allusion to the natural origin of nitrate of potassium. *Sal prunella* (from *sal*, a salt, and *pruna*, a live coal) is nitrate of potassium melted over a fire and cast into cakes or bullets.

The nitric radical is univalent (NO_3').

Constitution of Salts.

It is here necessary again to caution the reader against regarding salts as invariably possessing a known constitution, or supposing that they always possess two or more sides, or contain definite radicals. The erroneous conception which, of all others, is most likely to be imperceptibly formed, is that of considering salts to be binary bodies. For, first, the names of salts are necessarily binary. A student hears the names "sulphate of iron," "sulphate of copper," and simultaneously receives the impression that each salt has two sides, copper or iron occupying one, and something indicated by the words "sulphate of" the other. Such words as "vitriol," green or blue, or "nitre," would perhaps implant unitary ideas in the mind; but it is simply impossible to give such names to all salts as will convey the impression that each salt is a whole, and therefore unitary. The name "sulphate of potash" produces binary impressions; and the less incorrect name, "sulphate of potassium," or "potassium sulphate," is in this respect no better. Secondly, it is impracticable to study salts as a whole. Teachers are almost unanimous in the opinion that students should first master the reactions characteristic of the metals in salts, and then the residues which, with those metals, make up the salts, and *vice versâ*. It is not only impracticable, but impossible, to study salts as a whole; binary ideas concerning them are therefore almost inevitably imbibed. We come to regard a salt as a body which splits up in one direction only; look upon nitre, for instance, and all other nitrates, as containing NO_3 and a metal, M; whereas KNO_3 may be split up into KNO_2 and O; or into K_2O, N_2, and O_5; or may contain K_2O and N_2O_5. These are the chief disadvantages attending the employment of the binary hypothesis in studying chemical compounds: if they be borne in mind, the hypothesis may be freely used without much danger of permanent mental bias. Thus, in nitre, let the group of elements (NO_3) which, with potassium, makes up the whole salt, be called the nitric radical, the name of the latter being directly derived from its hydrogen salt. Similarly allow the acidulous residues of other salts of metals to be termed respectively the chloric, acetic, sulphurous, sulphuric, carbonic, oxalic, tartaric, phosphoric, citric, boracic radicals. In short, these compound radicals should be regarded as groupings common to many salts, and which may usually be transferred without any apparent breaking or splitting; at the same time we must be prepared to find that occasionally a salt divides in other directions. In this way perhaps erroneous impressions will gain least hold on the mind, and a way be left open for the easy entrance of new truths, should the real constitution of salts be discovered.

Formerly salts (such as sulphate of magnesium) were regarded as containing (*a*) an oxide of a metal (MgO) and an anhydride (SO_3), the latter being incorrectly called an acid (sulphuric acid); or (*b*) as containing two simple radicals (*e.g.* KI, $NaCl$, KCy, HgS)—the former being called *oxyacid salts* or *oxysalts*, and the latter *haloid salts* (from ἅλς, *als*, sea-salt, and εἶδος, *eidos*, likeness). Such distinction is no longer maintained, the two classes being merged. This is an important educational gain on the side of simplicity; for whereas under the old system much time was necessarily expended before salts of a metal and salts of the oxide of that metal could be distinguished (*e.g.* KI and K_2O, SO_3), now, all salts being regarded as salts of the metals themselves (*e.g.* KI and K_2SO_4), no such distinction is necessary.

REACTIONS.

Nitric Acid.

Synthetical Reaction.—To a fragment of nitrate of potassium or nitrate of sodium in a test-tube add a drop or two of sulphuric acid, and warm; nitric acid (HNO_3) is evolved in vapour. The fumes may be condensed by a bent tube fitted to the test-tube, not by a cork as for hydrochloric acid —because the nitric vapours would strongly act on it—but by plaster of Paris, a paste of which sets hard on being put aside for a short time, and is unaffected by the acid.

On a somewhat larger scale, nitric acid may be prepared by heating, in a stoppered or plain retort, a mixture of equal weights of nitrate of potassium and sulphuric acid; the acid distils over, and acid sulphate of potassium remains behind:—

$$\underset{\substack{\text{Nitrate of}\\ \text{potassium.}}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3} + \underset{\substack{\text{Acid sulphate}\\ \text{of potassium.}}}{KHSO_4}$$

Half the quantity of sulphuric acid may be taken; but in that case neutral sulphate of potassium (K_2SO_4) is produced, which, from its hard, slightly soluble character, is removed with difficulty from the retort. On the manufacturing scale, the lesser proportion is used; but instead of retorts iron cylinders are employed, from which the residual salt is removed by chisels. Moreover, the cheaper sodium salt is the nitrate from which manufacturers usually prepare nitric acid, seven parts of nitrate of sodium and four of sulphuric acid being employed.

Note.—The acid sulphate of potassium is readily converted into neutral sulphate (*Potassii Sulphas*, B.P.) by dissolving in water, adding carbonate of potassium until effervescence ceases to occur, filtering, and setting aside to crystallize.

Pure nitric acid (HNO_3) is a colourless liquid, somewhat difficult of preparation; its specific gravity is 1·52. The strongest acid met with in commerce has a sp. gr. of 1·5 and contains 93 per cent. of real nitric acid (HNO_3); it fumes disagreeably, is unstable, and, except as an escharotic, is seldom used. The British Pharmacopœia contains two acids: —*Acidum Nitricum*, prepared as above, of sp. gr. 1·42, and containing 70 per cent. of real acid (HNO_3); and another, *Acidum Nitricum Dilutum*, sp. gr. 1·101, containing nearly 17½ (17·44) per cent. Either of the stronger liquids, although containing water, is usually simply termed "nitric acid." The official nitric acid, of sp. gr. 1·42, is a definite hydrous acid ($2HNO_3, 3H_2O$); it distils at 240° F. without change. If a weaker acid be heated, it loses water; if a stronger acid be heated, it loses nitric acid, until the density of 1·42 is reached. *Aqua fortis* is an old name for nitric acid (*Aqua fortis simplex*, sp. gr. 1·22 to 1·25; *Aqua fortis duplex*, 1·36). The strength of a specimen of nitric acid is determined by volumetric analysis. *Nitric anhydride* (N_2O_5), sometimes, but erroneously, called *anhydrous nitric acid*, is a solid crystalline substance formed on passing dry chlorine over dry nitrate of silver.

Metals reduce nitric acid to nitrous acid and to the various oxides of nitrogen or even to nitrogen itself, according to the strength of acid, temperature, and amount of nitrate present. Not infrequently nitrate of ammonium is simultaneously formed. Thus, with zinc,—

$$10HNO_3 + 2Zn_2 = 4(Zn2NO_3) + NH_4NO_3 + 3H_2O.$$

Aqua Regia.—Three fluid ounces of nitric acid (B.P.), four of hydrochloric acid (B.P.), and twenty-five of water form the *Acidum Nitrohydrochloricum Dilutum* of the British Pharmacopœia. The mixture should be set aside for a week in summer or a fortnight in winter, to insure mutual decomposition and full development of the chief active product, chlorine :—

$$\begin{array}{ccccccccc} 2HNO_3 & + & 6HCl & = & N_2O_2Cl_4? & + & 4H_2O & + & Cl_2. \\ \text{Nitric acid.} & & \text{Hydrochloric acid.} & & \text{Chloronitric gas.} & & \text{Water.} & & \text{Chlorine.} \end{array}$$

In the latter stages of the reaction, the decomposition expressed in the following equation also probably occurs :—

$$\begin{array}{ccccccccc} HNO_3 & + & 3HCl & = & NOCl & + & 2H_2O & + & Cl_2. \\ \text{Nitric acid.} & & \text{Hydrochloric acid.} & & \text{Chloronitrous gas.} & & \text{Water.} & & \text{Chlorine.} \end{array}$$

The undiluted mixture of acids is known as *aqua regia*, from its property of dissolving gold, the "king of metals."

"Diluted nitrohydrochloric acid" may attack organic matter with evolution of nitrous gases, hence should not be dispensed with tinctures, etc., without further dilution.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To a solution of any nitrate (*e.g.* KNO_3) add sulphuric acid, and then copper turnings, and warm; colourless nitric oxide gas (NO) is evolved, which at once unites with the oxygen in the tube, giving *red fumes* of nitric peroxide or peroxide of nitrogen (NO_2).

$$2KNO_3 + 5H_2SO_4 + Cu_3 = 2NO + 3CuSO_4 + 4H_2O + 2KHSO_4\text{; then } 2NO + O_2 = 2NO_2.$$

Performed on a larger scale, in a vessel to which a delivery-tube is attached, the reaction of nitric acid on copper becomes of synthetical interest, being the process for the preparation of nitric oxide gas for the purposes of chemical experiment.

Small amounts of a nitrate may be overlooked by this test, the colour of the red fumes not being very intense.

Undiluted nitric acid poured on to copper turnings gives dense red vapours of *nitrous acid* (HNO_2), *nitrous anhydride* (N_2O_3), *nitric peroxide* (NO_2), *nitric oxide* (NO), and even *nitrogen* (N_2), the reaction varying somewhat according to the temperature of the mixture and (Ackworth) the amount of nitrate of copper in solution. With ordinary copper, diluted nitric acid gives nitric oxide, $Cu_3 + 8HNO_3 = 3(Cu2NO_3) + 4H_2O + 2NO$.

Second Analytical Reaction.—To a cold solution of a nitrate, even if very dilute, add three or four crystals of sulphate of iron, shake gently for a minute, in order that some of the sulphate may become dissolved, and then pour eight or ten drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the vessel; a reddish purple or black coloration will appear between the acid and the supernatant liquid.

This is a very delicate test for the presence of nitrates. Nitrites give the reaction without the sulphuric acid. The black colour is due to a solution or, perhaps, combination of nitric oxide with a portion of the ferrous salt. The nitric oxide is liberated from the nitrate by the reducing action of the hydrogen of the sulphuric acid, the sulphuric radical of which is absorbed by another portion of the ferrous sulphate, the latter then becoming ferric sulphate.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 4H_2O + 3(Fe_23SO_4) + 2NO.$$

The process of oxidation is one frequently employed in experimental chemistry; and nitrates, from their richness in oxygen, but more especially because always at hand, are the oxidizers usually selected for the purpose. In the operation they generally split up in one way, namely into oxide of their basylous radical, nitric oxide gas, and available oxygen. Thus hydrogen nitrate (nitric acid) commonly yields oxide of hydrogen (water) and the other bodies mentioned, as shown in the following equation :—

$$4HNO_3 = 2H_2O + 4NO + 3O_2.$$

When nitrates, other than nitric acid, are used for the purpose of oxidation, a stronger acid, generally sulphuric, is commonly added in order that nitric acid may be formed, the hydrogen nitrate splitting up more readily than other nitrates.

The five oxides of nitrogen have now been mentioned, namely :—

$$\left.\begin{array}{ll} \text{Nitrous oxide} \ldots\ldots\ldots & N_2O \\ \text{Nitric oxide*} \ldots\ldots\ldots & NO \\ \text{Nitrous anhydride} \ldots\ldots & N_2O_3 \\ \text{Nitric peroxide*} \ldots\ldots & NO_2 \\ \text{Nitric anhydride} \ldots\ldots & N_2O_5 \end{array}\right\} \text{or} \left\{\begin{array}{l} N_2O \\ N_2O_2 \\ N_2O_3 \\ N_2O_4 \\ N_2O_5 \end{array}\right.$$

Nitrous oxide is a colourless gas, not altered on exposure to air; nitric oxide is also colourless, but gives red fumes in the air; nitrous anhydride is a red vapour condensible to a blue liquid; nitric peroxide is a red vapour condensible to an orange liquid; nitric anhydride is a colourless crystalline solid. The two anhydrides, by absorbing water, yield respectively nitrous acid (HNO_2) and nitric acid (HNO_3). Nitrous oxide is also probably an anhydride, the acid of which would doubtless have the formula HNO, while the silver and sodium salts certainly have the formulæ $AgNO$ and $NaNO, 3H_2O$ (Divers; Menke). The above series of compounds forms a good illustration of the doctrine of multiple proportions (p. 46).

Third Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red-hot; now place on the spot a fragment of a nitrate; deflagration ensues.

This reaction does not distinguish nitrates from chlorates. It is sufficient for the recognition of very small quantities of either class of salts, especially when they are mixed with other substances.

Gunpowder is an intimate mechanical mixture of 75 parts of nitre, 15 to 12½ parts of charcoal, and 10 to 12½ parts of sulphur. In burning it may be said to give sulphide of potassium (the white smoke, K_2S), nitrogen (N), carbonic oxide (CO), and carbonic acid (CO_2) gases, though the decomposition is seldom complete. The sudden production of a large quantity of highly heated gas from a small quantity of a cold solid is sufficient to account for all the effects of gunpowder.

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* The specific gravities of these gases indicate that NO and NO_2 are the correct formulæ, and not N_2O_2 and N_2O_4.

Fourth Analytical Reaction.—To nitric acid or other nitrate add solution of "sulphate of indigo;" the colour (indigotin-disulphonic-acid, $C_{16}H_8(HSO_3)_2N_2O_2$) is discharged.

"*Solution of Sulphate of Indigo*," B.P. (Sulphindylic or Sulphindigotic Acid), is made by digesting 5 grains of dry finely powdered indigo in a small quantity of strong sulphuric acid in a test-tube for an hour, the mixture being kept hot by a water-bath; the blue liquid is then poured into 10 ounces of sulphuric acid, the whole well shaken, set aside, and the clear liquid decanted. Free chlorine also destroys the colour of this reagent.

Indigo, B.P. ($C_{16}H_{10}N_2O_2$), is a blue colouring-matter deposited when infusion of various species of *Indigofera* is exposed to air and slight warmth. Under these circumstances, *indican*, a yellow, transparent, amorphous substance, soluble in water, breaks up into indigo, which is insoluble and falls as a sediment, and a sort of sugar termed *indiglucin*. The indigo is collected, drained, pressed, and dried. By action of deoxidizing agents indigo is converted into soluble colourless *indigogen*, *reduced indigo*, or *indigo white:* 1 part of powdered indigo, 2 of green sulphate of iron, 3 of slaked lime, and 200 of water, shaken together and set aside in a well-closed bottle, gives this *colourless indigo* ($C_{16}H_{12}N_2O_2$). A piece of yarn, calico or similar fabric, dipped into such a solution and exposed to air, becomes dyed blue, deposition of insoluble indigo-blue occurring within the cells and vessels of the fibre. This operation is readily performed on the small scale, and forms an illustration of a characteristic feature of the art of dyeing—namely, the introduction of soluble colouring-matter into a fabric by permeation of the walls of its cellular and vascular tissue, and the imprisonment of that colouring-matter within the cells and vessels by conversion into a solid and insoluble form (*vide* also page 156). Indigo is probably a derivative of benzene.

Pure indigo, or *indigotin*, may be obtained in beautiful needles by spreading a paste of indigo and plaster of Paris on a tin plate, and when quite dry placing a lamp underneath, moving the latter from place to place as the indigo sublimes and condenses on the surface of the plaster. It may also be obtained in crystals by gently boiling finely powdered indigo with aniline, filtering while hot, and setting aside; these crystals may be washed with alcohol. Hot paraffin may be employed instead of aniline. Indigo may be produced artificially. Toluene, from coal-tar, is, by Perkin's process, converted into cinnamic acid, this into a nitro-derivative, and this again into orthonitrophenylpropiolic acid. From the latter, alkali and grape sugar deposit crystalline indigo (Baeyer).

Distinction between nitric acid and other nitrates.—Presence of the nitric radical in a solution having been proved by the above reactions, its occurrence as the nitrate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper and the detection of the metal—its occurrence as nitric acid by the sourness of the liquid to the taste, and the strong effervescence produced on the addition of a carbonate.

Antidote.—In cases of poisoning by strong nitric acid, solution of carbonate of sodium (common washing soda) or magnesia and water may be administered as antidotes.

QUESTIONS AND EXERCISES.

Trace the origin of nitrates.—In what does cubic nitre differ from prismatic nitre?—Describe a process by which nitrate of potassium may be obtained artificially.—State the difference between nitrate of potassium, nitre, saltpetre, and sal prunella.—What group of elements is characteristic of all nitrates? and what claim has this group to the title of radical?—Mention the usual theory regarding the manner in which atoms are arranged in reference to each other in such salts as nitrate of potassium.—How is the official nitric acid prepared?—Give the properties of nitric acid.—What reactions occur when strong nitric and hydrochloric acids are mixed?—How is nitric oxide prepared?—Enumerate and explain the tests for nitrates.—Into what substances does nitric acid usually split when employed as an oxidizing agent?—How is nitrous oxide prepared?—Enumerate the five oxides of nitrogen.—What is the nature of gunpowder?—Write a few sentences on the chemistry of indigo, one of the tests for nitric acid.—How is nitric acid distinguished from other nitrates?—What quantity of cubic nitre will be required to produce ten carboys of official nitric acid, each containing 114 lbs.? *Ans.*, 1,076⅔ lbs.

CHLORIC ACID AND OTHER CHLORATES.

Formula of the Acid, $HClO_3$ or ClO_2OH. Molecular weight, 84·5. Chlorates (p. 342) are made from hypochlorites.

Hypochlorous Acid ($HClO$ or $ClOH$) and other Hypochlorites.

Place a few grains of red oxide of mercury in a test-tube, half fill the tube with chlorine water, and well shake the mixture; the resulting liquid is a solution of hypochlorous acid, mercuric oxychloride remaining undissolved:—

$$2HgO + 2Cl_2 + H_2O = 2HClO + Hg_2OCl_2.$$

By the metathesis (double decomposition) of hypochlorous acid and oxides or hydrates, other pure hypochlorites are formed:—$HClO + NaHO = NaClO + H_2O$.

The direct action of chlorine on metallic hydrates and some carbonates is supposed to give a compound of chloride and hypochlorite, as described in connection with the synthetical reactions of calcium (page 125, *Calx Chlorinata*, B.P.). (See also page 93, *Liquor Sodæ Chlorinatæ*, B.P.)

$$\begin{aligned} Cl_2 + 2NaHO &= NaCl, NaClO + H_2O; \\ 2Cl_2 + 2CaH_2O_2 &= CaCl_2, Ca2ClO + 2H_2O. \end{aligned}$$

The condition of the chlorine in these bodies is not satisfactorily made out; so that their constitution is not definitely determined. The action of acids on them results in the evolution of chlorine; hence the great value of the calcium compound (chlorinated lime, or chloride of lime) in bleaching operations:—

$$CaCl_2, Ca2ClO + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O.$$

The solubility of hypochlorites in water, their peculiar odour, greatly intensified on the addition of acid, and their bleaching powers (*see* the above calcium reaction) are the characters on which to rely in searching for hypochlorites.

Chlorates.

The group of elementary atoms represented by the formula ClO_3 is that characteristic of chloric acid and all other chlorates; hence it is expedient to regard it as being an acidulous radical, which may be termed the chloric radical. Like the nitric radical, it has not been isolated. Chloric anhydride (Cl_2O_5), unlike nitric anhydride, has not yet been obtained in the free condition.

Chlorates are artificial salts. They are formed by simply boiling aqueous solutions of the common bleaching salts (chlorinated lime, chlorinated soda, chlorinated potash). Heat thus converts—

$3(NaCl, NaClO)$ Chlorinated soda.	into	$NaClO_3$ Chlorate of sodium.	and	$5NaCl$ Chloride of sodium.
$3(KCl, KClO)$ Chlorinated potash.	into	$KClO_3$ Chlorate of potassium.	and	$5KCl$ Chloride of potassium.
$3(CaCl_2, Ca2ClO)$ Chlorinated lime.	into	$Ca2ClO_3$ Chlorate of calcium.	and	$5CaCl_2$ Chloride of calcium.

One chlorate may also be made from another by double decomposition. In making chlorates economically the chlorinated salt is, of course, at once converted into chlorate.

Chlorate of Potassium.

Thus, Chlorate of Potassium (*Potassii Chloras*, B.P.), the old Chlorate of Potash, is commercially made by saturating with chlorine gas a moistened mixture of 3 parts of chloride of potassium and 10 of slaked lime, and well boiling the product. Chlorinated lime is first formed; this, on continued boiling with water, splits up into chloride of calcium and chlorate of calcium; and the latter reacting on the chloride of potassium yields chloride of calcium and chlorate of potassium.

$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2, Ca2ClO) + 6H_2O:$$
$$3(CaCl_2, Ca2ClO) = Ca2ClO_3 + 5CaCl_2;$$
$$Ca2ClO_3 + 2KCl = CaCl_2 + 2KClO_3.$$

The operation may be conducted on a small scale by rubbing together in a mortar the above proportions of ingredients in ounces or half-ounces, adding enough water to make the whole assume the character of damp lumps, placing the porous mass in a funnel (loosely plugged with stones or pieces of glass) and passing chlorine gas (p. 21) up through the mass by attaching the tube delivering the gas to the neck of the funnel. When the whole mass has become of a slight pink tint (due to a trace of permanganate) it should be turned into a dish, *well* boiled with water, filtered, the filtrate evaporated if necessary, and set aside; the chlorate of potassium crystallizes out in colourless rhomboidal plates, chloride of calcium remaining in the mother-liquor.

In the official process, carbonate of potassium is alluded to as being used in place of chloride; but otherwise the method is similar to that just described. Chlorinated potash and chlorinated lime are first formed—

$$K_2CO_3 + Ca2HO + Cl_2 = KCl, KClO + CaCO_3 + H_2O$$
$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2, Ca2ClO) + 6H_2O;$$

these on boiling with water split up into chlorates and chlorides—

$$3(KCl, KClO) = KClO_3 + 5KCl$$
$$3(CaCl_2, Ca2ClO) = Ca2ClO_3 + 5CaCl_2,$$

the whole of the chloride of potassium and chlorate of calcium finally yielding chlorate of potassium and chloride of calcium,—

$$2KCl + Ca2ClO_3 = CaCl_2 + 2KClO_3.$$

Neglecting intermediate decompositions, the reactions may be represented by the following equation:—

$$\underset{\text{Chlorine.}}{6Cl_2} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} + \underset{\text{Hydrate of calcium.}}{6CaH_2O_2} =$$
$$\underset{\text{Chlorate of potassium.}}{2KClO_3} + \underset{\text{Carbonate of calcium.}}{CaCO_3} + \underset{\text{Chloride of calcium.}}{5CaCl_2} + \underset{\text{Water.}}{6H_2O}$$

Chlorate of Sodium (*Sodii Chloras*, U.S.P.), $NaClO_3$, is similarly prepared.

Chlorate of potassium is soluble in water to the extent of 6 or 7 parts in 100 at common temperatures. It is usually administered medicinally in aqueous solution, sometimes also in lozenges (*Trochisci Potassii Chloratis*, B.P.). Chlorate of potassium must on no account be rubbed with sulphur or sulphides, in a mortar or otherwise, friction of such a mixture resulting in violent explosion.

Chlorate of potassium, when heated, yields chloride of potassium and oxygen, and is the salt commonly employed in the preparation of the gas for experimental purposes. But if the action be carried on at as low a temperature as possible, and be arrested when one hundred parts of the chlorate have (Teed) yielded 7·84 parts of oxygen, the residual salt will be found to contain only perchlorate of potassium ($KClO_4$) and chloride; $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$. A higher temperature causes the decomposition of the perchlorate; $KClO_4 = KCl + 2O_2$. When the chlorate is heated with peroxide of manganese, no perchlorate is formed.

Perchloric acid ($HClO_4$).—Crude perchlorate of potassium obtained as just indicated, is boiled (in a fume-cupboard) with hydrochloric acid to decompose any chlorate that may be remaining, and then separated from chloride by washing and crystallization, chloride being far more soluble in water than perchlorate. Perchloric acid is then obtained by distilling the perchlorate of potassium with sulphuric acid; it is stable, and is occasionally administered in medicine.

Chloric acid ($HClO_3$) may be isolated, but is unstable, quickly decomposing into chlorine, oxygen, and perchloric acid; some other chlorate (*e.g.* $KClO_3$) must therefore be used in studying the reactions of the chloric radical.

Table of the Chlorine Acids.

Hydrochloric acid	HCl.
Hypochlorous acid	$HClO$.
Chlorous acid.	$HClO_2$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

The chloric radical is univalent (ClO_3'). The acidulous radicals of the other chlorine acids are also univalent, as indicated in the foregoing formulæ.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To solution of a chlorate (*e.g.* chlorate of potassium) add solution of nitrate of silver; no precipitate falls, showing that the chlorine must be performing different functions from those it possesses in chlorides. Evaporate the solution to dryness, and place the residue in a small dry test-tube, or at once drop a fragment of a chlorate into a test-tube, and heat strongly; oxygen is evolved, and may be recognised by its power of reinflaming an incandescent match inserted in the tube. Boil the residue with water, and again add solution of nitrate of silver; a white precipitate falls, having all the characters of chloride of silver, as described under hydrochloric acid.

Second Analytical Reaction.—To a fragment of a chlorate add two or three drops of strong sulphuric acid; an explosive gas (Cl_2O_4) is evolved, somewhat resembling chlorine in odour, but possessing a deeper colour than that element.

$$3KClO_3 + H_2SO_4 = Cl_2O_4 + KClO_4 + K_2SO_4 + H_2O.$$

Warm the upper part of the test-tube to 150° or 200° F., or introduce a hot wire; a sharp explosion ensues, due to decomposition of the gas, peroxide of chlorine, into its elements.

Third Analytical Reaction.—Heat a small fragment of a chlorate with hydrochloric acid; a yellowish-green explosive gas, termed *euchlorine*, is evolved. Its colour is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρὸς, *chlōros*, green). In odour it resembles chlorine, and is probably a mixture of that element with one of the oxides of chlorine.

Fourth Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red-hot, and then place on the spot a fragment of a chlorate; deflagration ensues, as with nitrates.

Bromates.

Bromates are salts closely resembling chlorates and iodates. The formula of Bromic Acid is $HBrO_3$. The presence of bromates in bromides is shown by the production of a yellow colour on the addition of diluted sulphuric acid.

$$5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3Br_2.$$

Iodates.

Iodic Acid (HIO_3).—Iodine is warmed in a flask with five times its weight of the strongest nitric acid (sp. gr. 1·5), in a fume-cupboard, until all action ceases. On cooling, iodic acid separates in small pyramidal crystals. These are removed, the residual liquid evaporated to dryness to remove excess of nitric acid, the residue and the first crop dissolved in a small quantity of boiling water, and the solution set aside to crystallize.

Iodate of Potassium (KIO_3).—Powder equal weights of iodine and chlorate of potassium; to the mixture add twice its weight of water and about one-eighth of its weight of nitric acid; warm the whole until iodine disappears, and evaporate to dryness over a water-bath. The residue, dissolved in water, forms the reagent "Solution of Iodate of Potassium." It contains nitrate of potassium.

In this reaction the small quantity of nitric acid furnishes corresponding amounts of nitrate of potassium and chloric acid. This chloric acid with iodine gives iodic acid and chlorine; thus:—$2HClO_3 + I_2 = 2HIO_3 + Cl_2$. The iodic acid and more chlorate of potassium then yield more chloric acid and iodate of potassium:—$HIO_3 + KClO_3 = HClO_3 + KIO_3$; and the two reactions alternate until the whole of the iodine has displaced the whole of the chlorine. But according to Millon, 1843, and Bassett, 1890, even still more complicated reactions occur.

Iodate of potassium and sulphurous acid decompose each other with elimination of iodine (or with formation of a blue colour, if starch be present). Sulphurous acid occurring as an impurity in acetic and other acids may thus be detected.

$$2KIO_3 + 5H_2SO_3 = I_2 + 3H_2SO_4 + 2KHSO_4 + H_2O.$$

Ferric Iodate, or rather *Oxyiodate* ($Fe_2O4IO_3, 8H_2O$), is precipitated on adding solution of ferric chloride to solution of iodate of potassium.

QUESTIONS AND EXERCISES.

How may hypochlorous acid be formed?—What are the relations of hypochlorous acid to bleaching-powder?—By what reaction is chlorine eliminated from hypochlorites?—State the general reaction by which chlorates are formed.—Give details of the preparation of chlorate of potassium.—Mention the properties of chlorate of potassium.—What decompositions occur when chlorate of potassium is heated?—Find the molecular weight of chlorate of potassium.—What weight of oxygen is yielded when 1 oz. of chlorate of potassium is completely decomposed? and how much chloride of potassium remains?—One hundred cubic inches of oxygen, at 60° F. and barometer at 30 inches, weighing 34·203 grains, and one gallon containing 277¼ cubic inches, what weight of chlorate of potassium will be required to yield 10 gallons of the gas? *Ans.*, 5½ oz.—How many cubic inches of oxygen are producible from 1 oz. of chlorate of potassium?—Calculate the weight of chlorate of potassium theoretically obtainable from 100 parts of chloride.—How is perchloric acid prepared?—Enumerate the chlorine acids.—How may the presence of chlorides in chlorates be demonstrated?—Mention the tests for chlorates.—Give the formula of peroxide of chlorine.—What is euchlorine?—How may iodic acid be made?—Describe the preparation of iodate of potassium.

ACETIC ACID AND OTHER ACETATES.

Formula of Acetic Acid, $HC_2H_3O_2$. Molecular weight, 60.

Source.—Acetic acid is said to occur naturally in certain plant-juices and animal fluids in minute proportions, but otherwise is an artificial product. Much is furnished by the destructive distillation of wood. When first discovered this was regarded as a new acid, and was named *pyroligneous acid*, a hybrid word from πῦρ, *pūr*, fire, and *lignum*, wood, a term still retained for the crude acid. The latter, neutralized by carbonate of calcium, the whole evaporated and the residue gently heated to drive off volatile tarry matters, gives acetate of calcium, which after conversion into acetate of sodium and recrystallization furnishes by distillation with sulphuric acid and water acetic acid in a state of purity. Diluted acetic acid is *white vinegar*, one of the now many varieties of *vinegar*. It has been known as *wood vinegar* for the past sixty years. It is generally coloured brown with caramel to meet the taste of the public. In Germany and France large quantities of acetic acid are made by the spontaneous oxidation of the alcohol in inferior wines, in the presence, according to Pasteur, of a plant-ferment termed *Mycoderma Aceti* (the *Bacterium Mycodermi* of Cohn); hence the *white-* and *red-wine vinegar* (*vinegar*, from the French *vin*, wine, and *aigre*, sour). Indeed, this bacterium may be propagated, and the artificial manufacture of vinegar from alcohol and water be carried out, by its aid, on a larger scale. In England also the domestic form of acetic acid (brown vinegar) commonly has an alcoholic origin: infusion of malt and unmalted grain, or sometimes the latter alone after treatment with sulphuric acid, is fermented; and the resulting alteration of its sugar, instead of being arrested when the product is an alcoholic liquid, a sort of beer, is allowed to go on to the next stage, acetic acid; it usually contains from 3 to 6 per cent. of real acetic acid ($HC_2H_3O_2$). Different strengths of vinegar are sold under the numbers, 16, 18, 20, 22, and 24, corresponding to the number of grains of anhydrous carbonate of sodium neutralized by one imperial fluid ounce of the vinegar. All of these "brewed vinegars" are further coloured, with caramel, to suit the popular taste. *Vinegar* is a generic term applicable to any one or to all varieties. Its essential component is acetic acid.

Official Vinegars.—The official "vinegar" (*Acetum*, B.P.) contains 5½ (5·41) per cent. of acid. The so-called Vinegar of Cantharides (*Acetum Cantharidis*, B.P.) is a solution of the active principle of cantharides in very strong acetic acid, not in official vinegar. The Vinegars of Squill (*Acetum Scillæ*, B.P.), and of Ipecacuanha (*Acetum Ipecacuanhæ*, B.P.), contain diluted acetic acid, that is, *wood vinegar*, not the official "vinegar," which is that made from malted and unmalted grain, commonly 1 part of the former to 3 of the latter. In the Pharmacopœia, "vinegar," except rare occasional use for its own sake, is only employed in the preparation of *Emplastrum Saponis Fuscum.*

The Acetic Radical.—The group $C_2H_3O_2'$ is that characteristic of acetic acid and other acetates. It is univalent.

Acetyl.—The characteristic group in acetates ($C_2H_3O_2$) is considered to contain, rather than to be, a radical—the radical C_2H_3O, termed *acetyl*. Acetates yield a body having the composition C_2H_3OCl, which is regarded as chloride of acetyl; from this may be obtained acetic anhydride ($C_4H_6O_3$), which, by absorbing water, becomes acetic acid.

$$\begin{array}{cccc} \left.\begin{matrix}C_2H_3O\\ Cl\end{matrix}\right\} & \left.\begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\right\}O & \left.\begin{matrix}C_2H_3O\\ H\end{matrix}\right\}O & \left.\begin{matrix}C_2H_3O\\ M'\end{matrix}\right\}O \\ \text{Chloride of acetyl.} & \text{Acetic anhydride.} & \text{Acetic acid.} & \text{Metallic acetates.} \end{array}$$

The quantitative relation of acetic acid to alcohol will be evident from the following equation, representing, empirically, the formation of the acid :—

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = \underset{\text{Acetic acid.}}{C_2H_4O_2} + H_2O.$$

Acetates in aqueous solution are liable to decomposition. In solution of acetate of morphine a myceloid growth occasionally forms, acetic acid disappears, and morphine is deposited. Solution of acetate of ammonium is liable to a similar change, gradually becoming alkaline.

SYNTHETICAL REACTION.

Acetic Acid.

To a few grains of acetate of sodium in a test-tube add a little water and some sulphuric acid, and heat the mixture; acetic acid is evolved, and may be condensed by a bent tube adapted to the test-tube by a cork in the usual way.

Acetic Acid.—This is the process by which acetate of sodium or calcium (the neutralized products of the distillation of wood) is made to yield acetic acid on the large scale. As with nitric and hydrochloric acids, the loose term "acetic acid" is that usually applied to aqueous solutions of acetic acid. The *Acidum Aceticum*, B.P., contains about 33 per cent. of real acid, that is, of $HC_2H_3O_2$; for it contains only 28 per cent. of *acetic anhydride* ($C_4H_6O_3$)—still occasionally, though somewhat obscurely, termed *anhydrous acetic acid*. *Acidum Aceticum Dilutum*, B.P., contains about $4\frac{1}{4}$ (4·27) per cent. of $HC_2H_3O_2$. Glacial acetic acid ($HC_2H_3O_2$) contains no water. It solidifies to a crystalline mass at temperatures below 63° F., hence the appellation *glacial* (from *glacies*, ice). Good commercial glacial acetic acid (*Acidum Aceticum Glaciale*, B.P.) does not contain more than 1 per cent. of water; it solidifies when cooled, and again liquefies at about 60°; its specific gravity is 1·058. Although water is lighter than this acetic acid, yet the addition of water at first renders the acid heavier; evidently, therefore, condensation, or contraction in bulk, occurs on mixing the liquids: after 10 per cent. has been added, the addition of more water produces the usual effect of dilution of a heavy liquid by a lighter—namely, reduction of relative weight. This matter will be better understood after the subject of specific gravity has been studied. Glacial acetic acid mixes readily with most oils.

The following equation shows the reaction:—

$$\underset{\text{Acetate of sodium.}}{NaC_2H_3O_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acetic acid.}}{HC_2H_3O_2} + \underset{\text{Acid sulphate of sodium.}}{NaHSO_4};$$

or, assuming the existence of acetyl (C_2H_3O) in acetic acid (united with hydroxyl, HO), and the radical sulphuryl (SO_2) in sulphuric acid (united with 2HO),

$$\left.\begin{array}{r}C_2H_3O\\ Na\end{array}\right\}O + \left.\begin{array}{r}SO_2\\ H_2\end{array}\right\}O_2 = \left.\begin{array}{r}C_2H_3O\\ H\end{array}\right\}O + \left.\begin{array}{r}SO_2\\ HNa\end{array}\right\}O_2;$$

or, on the assumption that salts contain the oxide of a basylous radical united with the anhydride of an acid (the old view under which such names as acetate of soda were formed),

$$Na_2O, C_4H_6O_3 + 2H_2O, SO_3 = Na_2O, H_2O, 2SO_3 + H_2O, C_4H_6O_3.$$

Note on the Constitution of Salts.

Which of these three equations, or, more broadly, which of the three views of the constitution of salts illustrated by the equations, is correct, is questionable. Whether it is $C_2H_3O_2$, C_2H_3O, or $C_4H_6O_3$, which migrates from one acetic compound to another, whether it is SO_4, SO_2, or SO_3, which migrates from one sulphuric compound to another, and so on with other acidulous groupings, cannot at present be determined. There are some objections to each view; and possibly neither is right. Either the given radicals cannot be isolated; or application of the forces of heat, light, and electricity do not confirm views arrived at by the results of operations with the chemical force; or a salt comes to be regarded as having so large a number of constituent parts, that the view breaks down from the sheer inability of students, at all events at the present stage of study, to grasp the complicated analogies involved. Yet for the purposes of description, study, and conversation, some system must be adopted. Let the first, then, be taken for the present, over-reliance on it being checked by the use of general instead of special names for the hypothetical radicals, and other systems be employed in other cases. (*See* also p. 333.)

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To an acetate add sulphuric acid, and heat the mixture; a characteristic odour (acetic acid) is evolved.

Note 1.—Iodine, sulphurous acid, and other substances of powerful odour, mask that of acetic acid; they must be removed, therefore, usually by precipitation or oxidation, before applying this test.

Note 2.—It will be noticed that this reaction is identical with the previous one; it has synthetical or analytical interest, according to the object and method of its performance.

Second Analytical Reaction.—Repeat the above reaction, a few drops of spirit of wine being first added to the acetate; acetic ether (acetate of ethyl, $C_2H_5C_2H_3O_2$), also of characteristic odour, is evolved. The basylous radical ethyl (C_2H_5) will be referred to subsequently.

Third Analytical Reaction.—Heat a fragment of a dry acetate in a test-tube, and again notice the odour of the gaseous products of the decomposition; among them is *acetone* (C_3H_6O), the smell of which is characteristic. Carbonate of the metal remains in the test-tube.

Fourth Analytical Reaction.—To a solution of an acetate, made neutral by the addition of acid or alkali, as the case may be, add a few drops of neutral solution of perchloride of iron; a deep-red liquid results, owing to the formation of ferric acetate ($Fe_26C_2H_3O_2$). Boil; a red precipitate (oxy-acetate of iron) occurs, leaving the liquid colourless.

Analytical Note.—It will be noticed that the formation of characteristic precipitates, the usual method of removing radicals from solution for recognition, is not carriod out in the qualitative analysis of acetates. This is because all acetates are soluble. Acetate of silver ($AgC_2H_3O_2$) and mercurous acetate ($HgC_2H_3O_2$) are only sparingly soluble in cold water, but the fact can seldom be utilized in analysis. Hence peculiarities of colour and odour, the next best characters on which to rely, are adopted as means by which acetates may be detected. Acetates, like other organic compounds, char when heated to a high temperature.

Note on Anhydrides.—Up to this point the student has regarded an anhydride as a body derived from an acid by removal of the *whole* of the hydrogen of the acid, together with as much of its oxygen as with the hydrogen forms water. This definition will scarcely apply to acetic anhydride, and must therefore be somewhat qualified. An *anhydride* is derived from an acid, the acid having lost the whole of its *basylous* hydrogen and so much oxygen as is necessary to form water with that hydrogen. Anhydrides are obtained by heating acids, and by other methods.

QUESTIONS AND EXERCISES.

What is the formula of acetic acid?—State the relation of acetic acid to other acetates.—What is the molecular weight of acetic acid?—Name the sources of acetic acid.—What is pyroligneous acid?—From what compound is the acetic acid of most foreign and English varieties of vinegar derived?—How much real acid is contained in official vinegar?—What is the nature of the "Vinegars" of Pharmacy?—How may acetic acid be obtained from acetate of sodium?—How much real acid is contained in the official acetic acid?—Mention the strength of commercial glacial acetic acid.—Give three or more views of the constitution of acetates, illustrating each by formulæ.—Enumerate the tests for acetates.

HYDROSULPHURIC ACID AND OTHER SULPHIDES.

Formula of Hydrosulphuric Acid, H_2S. Molecular weight, 34.

Source and varieties of Sulphur.—The acidulous radical of *hydrosulphuric acid*, *sulphydric acid*, or *sulphuretted hydrogen* and other sulphides, is the element sulphur (S). It occurs in nature in the free condition, also in combination with metals, as already stated in describing the ores of some of the metals. The coal-gas industry furnishes much sulphur as a by-product, it occurring in coal, chiefly as iron pyrites.

Most of the sulphur used in medicine is imported from Sicily, where it occurs chiefly associated with blue clay. It is purified by fusion, sublimation, or distillation. Melted and poured into moulds, it constitutes a crystalline mass termed *roll sulphur*. If distilled and the vapour carried into large chambers, so that it may be rapidly condensed, the crystals are so minute as to give the sulphur a pulverulent character; this is *sublimed sulphur* (*Sulphur Sublimatum*, B.P.), or *flowers of sulphur:* the same washed with dilute ammonia, to remove the traces of sulphuric acid (often 0·1 per cent., resulting from very slow oxidation of sulphur in ordinary moist air), or, possibly, arsenious sulphide, constitutes *Sulphur Lotum*, U.S.P. The third common form, *milk of sulphur*, will be noticed subsequently. Sulphur also occurs in nature in combination as a constituent of animal and vegetable tissues, as sulphurous acid gas (SO_2) in volcanic vapours, and as sulphuretted hydrogen in some mineral waters. *Plastic sulphur* is one of the allotropic varieties of the element, obtained on heating sulphur considerably beyond its melting-point, and pouring into cold water.

Quantivalence.—Sulphur would seem to be sexivalent in sulphuric anhydride (SO_3), a substance which will be noticed under sulphuric acid, and quadrivalent in sulphurous anhydride (SO_2), while it still oftener exhibits bivalent affinities (H_2S).

Molecular weight.—At very high temperatures sulphur follows the rule that, under similar conditions of heat and pressure, molecular weights (in grammes, grains, etc.) of volatile elements occupy equal volumes of vapour; its formula therefore is S_2, and molecular weight 64. At lower temperatures the volume weighs three times as much as it should do if following usual laws, and then the molecule would appear to contain six atoms (S_6).

Acid Salts.—Sulphur (S'') being the first acidulous radical of bivalent activity met with in these sections on acids, it is desirable here to draw attention to a new class of salts to which such a radical will give rise. These are acid salts (as $KHSO_4$) which are intermediate between neutral salts (as K_2SO_4) and acids (as H_2SO_4). Univalent acidulous radicals, with an atom of hydrogen, give an acid, and with an atom of other basylous radicals an ordinary or neutral salt. But bivalent acidulous radicals, inasmuch as they give with two atoms of hydrogen an acid, and with two atoms of univalent metals a neutral salt, may obviously give intermediate bodies containing one atom of hydrogen and one atom of metal; these are appropriately termed acid salts: they are neither normal acids nor neutral salts, but *acid salts*. (Examples:—$KHCO_3$, $NaHSO_4$, $KHC_4H_4O_6$, Na_2HPO_4, $CuHAsO_3$, CaH_42PO_4.) Whether or not these and other salts give an acid reaction with blue litmus-paper depends on the strength of the respective radicals. Usually they do redden the test-paper, but sometimes not; thus the acid sulphide or sulphydrate of potassium (KHS), or sodium (NaHS), or ammonium (NH_4HS), has alkaline properties.*

The chemical analogy between sulphur and oxygen, already once alluded to (p. 199), is further illustrated by the compounds just mentioned. Thiacetic acid ($CH_3{\cdot}CO{\cdot}SH$) exists, and other *thio* (*θεῖον*, *theion*, sulphur) acids. Sulphur is also closely related to the rarer element selenium. Thus we have SeO_2 (selenious anhydride) as well as SO_2 (sulphurous anhydride), H_2SeO_3 (selenious acid) as well as H_2SO_3 (sulphurous acid), H_2SeO_4 (selenic acid) as well as H_2SO_4 (sulphuric acid). The rare element tellurium also seems to have similar analogies. The four hydrogen compounds of the group have the formulæ H_2O, H_2S, H_2Se, H_2Te. (*Vide* Index, "Periodic Law.")

SYNTHETICAL REACTIONS.

Sulphuretted Hydrogen.

First Synthetical Reaction. The preparation of sulphuretted hydrogen.—This operation was described on page 105, and probably has already been studied by the reader.

Precipitated Sulphur.

Second Synthetical Reaction.—Prepare the variety of the radical of sulphides known as *Precipitated Sulphur* (*Sulphur Præcipitatum*, B.P.), or *Milk of Sulphur*, by boiling a few grains of flowers of sulphur (5 parts) with slaked lime (3 parts) and some water (20 parts) in a test-tube (larger quantities in an evaporating-basin), filtering, and (reserving a small portion of the filtrate) adding diluted hydrochloric acid until the well-stirred milk-like liquid still has a faint alkaline or scarcely acid reaction on test-paper; sulphur is precipitated, and may be collected on a filter, washed, and dried (at about 130° F.). Excess of acid must be avoided, or some hydrosulphyl, the liquid persulphide of hydrogen (H_2S_2), will be formed, probably causing the particles of sulphur to aggregate to a gummy mass.

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* Chemists regard these sulphydrates as compounds of basylous radicals with HS, a univalent grouping termed hydrosulphyl (persulphide of hydrogen, H_2S_2), just as hydrates are similarly viewed as compounds of the univalent radical hydroxyl (HO) (peroxide of hydrogen, H_2O_2),—H_2S becoming HHS (hydrosulphylide of hydrogen), and H_2O becoming HHO (hydroxylide of hydrogen).

This is the process of the Pharmacopœia. Polysulphide of calcium and hyposulphite of calcium are formed :—

$$\underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{3CaH_2O_2} + \underset{\text{Sulphur.}}{6S_2} = \underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}$$

On adding the acid, both salts are decomposed and, after an intermediate reaction, sulphur separates :—

$$\underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl} = \underset{\substack{\text{Chloride of}\\ \text{calcium.}}}{3CaCl_2} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Sulphur.}}{6S_2}$$

The polysulphide of calcium yields sulphuretted hydrogen and milk-white sulphur on the addition of acid. The hyposulphite of calcium then yields sulphurous acid gas as well as yellowish sulphur. The gases react and give sulphur and water, very little sulphuretted hydrogen escaping: this is the intermediate reaction just alluded to. A little pentathionic acid (*see* Index) is also said to be formed.

$$4H_2S + 2SO_2 = 3S_2 + 4H_2O.$$

Sulphur Lozenges (*Trochisci Sulphuris*, B.P.) contain, each, 5 grains of precipitated sulphur, 8 grains of sugar, 1 grain of gum and of cream of tartar, and 1 minim of mucilage and of tincture of orange peel.

Calcareous Precipitated Sulphur. The *old* "Milk of Sulphur."—To a sulphur solution prepared as before (or to the reserved portion) add a little diluted sulphuric acid; the precipitate is in this case largely mixed with sulphate of calcium:—

$$\underset{\substack{\text{Polysulphide}\\ \text{of calcium.}}}{2CaS_5} + \underset{\substack{\text{Hyposulphite}\\ \text{of calcium.}}}{CaS_2O_3} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{3H_2SO_4} + \underset{\text{Water.}}{5H_2O} = \underset{\text{Sulphate of calcium.}}{4\,(CaSO_4,2H_2O)} + \underset{\text{Sulphur.}}{6S_2}$$

Place a little of each of these specimens of "precipitated sulphur," with a drop of the supernatant liquid, on a strip of glass, cover each spot with a piece of thin glass, and examine the precipitates under a microscope; the pure sulphur will be found to consist of minute grains or globules, the calcareous to contain comparatively large crystals (hydrous sulphate of calcium).

Note.—Some of the precipitated sulphur met with in trade is, in England, still thus mixed with sulphate of calcium, most of such specimens containing two-thirds of their weight of that substance. Formerly, purchasers were so accustomed to the satiny appearance of the mixed article as to regard real sulphur with suspicion, sometimes refusing to purchase it. The mixed article is, certainly, somewhat more easily miscible with aqueous liquids.

Calcareous precipitated sulphur yields a white ash (the anhydrous sulphate of calcium) when a little is burnt off on the end of a table-knife or spatula or in a crucible. (No more damage is done to the steel than a rub on a knife-board will remove.) To ascertain, exactly, the amount of the sulphate, place a weighed quantity in a tared crucible, and heat till no more vapours are evolved. The weight of the residual anhydrous sulphate of calcium ($CaSO_4 = 136$), with one-fourth thereof added, is the amount of crystalline sulphate of calcium ($CaSO_4, 2H_2O = 172$) present in the original quantity of calcareous sulphur.

ANALYTICAL REACTIONS (TESTS).

To a sulphide add a few drops of hydrochloric acid; sulphuretted hydrogen will probably be evolved, well known by its smell. If the sulphide is not acted upon by the acid, or if free sulphur be under examination, mix a minute portion with a fragment of solid caustic potash or soda, and fuse on a silver coin or old spoon. When cold, place a drop of dilute hydrochloric acid on the spot; sulphuretted hydrogen is evolved, and a black stain, due to sulphide of silver (Ag_2S), is left on the coin.

Other sulphur reactions may be adapted as tests; but the above are sufficient for all ordinary purposes. The most convenient reagent for detecting a sulphide in solution of ammonia is ammonio-sulphate of copper, which gives a black precipitate (sulphide of copper) if a sulphide be present.

The *Iodide of Sulphur* (S_2I_2) has been mentioned under "Iodine." A *chloride* (S_2Cl_2) and *bromide* (S_2Br_2) may also be formed from their elements. A mixture of sulphur and chloride of sulphur is sometimes met with under the name of *hypochloride of sulphur.*

QUESTIONS AND EXERCISES.

In what forms does sulphur occur in nature?—State the modes of preparation of the three chief commercial varieties of sulphur.—To what extent does the atom of sulphur vary in quantivalence?—State the relations of acid salts to acids and to normal salts.—Define sulphides and sulphydrates.—Describe the preparation of sulphuretted hydrogen. What are the characters of pure precipitated sulphur?—Give equations explanatory of the reactions which occur in precipitating sulphur according to the official process.—Describe the microscopic test for calcareous precipitated sulphur.—Mention a ready physical method of detecting sulphate of calcium in precipitated sulphur.—Mention the tests for sulphides, and the character by which sulphuretted hydrogen is distinguished from other sulphides.—How are sulphides insoluble in acids tested for sulphur? How would you detect a trace of sulphur in ammonia solutions?

SULPHUROUS ACID AND OTHER SULPHITES.

Formula of sulphurous acid, H_2SO_3. Formula of sulphurous acid gas or sulphurous anhydride, sometimes termed sulphurous acid, SO_2. Molecular weight of sulphurous acid, 82; of the anhydride, 64.

When sulphur is burnt in the air, it combines with oxygen and forms sulphurous acid gas (SO_2), more correctly termed sulphurous anhydride, or occasionally, but erroneously, sulphurous acid. It is a pungent, colourless gas, readily liquefied on being passed through a tube externally cooled by a *freezing-*

mixture composed of two parts of well-powdered ice (or, better, snow) with one part of common salt. If sulphurous acid gas becomes moist or is passed into water, heat is evolved and true sulphurous acid (H_2SO_3) is formed. The latter body may be obtained in crystals by freezing a strong aqueous solution; but it is very unstable, and hence the properties of the sulphurous radical must be studied under the form of some other sulphite; sulphite of calcium ($CaSO_3$), or sulphite of sodium (Na_2SO_3), may be used for the purpose.

Quantivalence.—The radical of the sulphites is bivalent (SO_3''), and hence forms acid sulphites, such as acid sulphite of potassium ($KHSO_3$), and neutral sulphites, such as sulphite of sodium (Na_2SO_3).

Note.—The sulphites are so named from the usual rule, that salts corresponding with acids whose names end in *ous* have a name ending in *ite*. They are generally made by passing sulphurous acid gas over moist oxides or carbonates; in the latter case carbonic acid gas escapes.

Synthetical Reaction.—To a few drops of sulphuric acid in a test-tube add a piece of charcoal and apply heat; sulphurous acid gas is evolved, and may be conveyed by a bent tube into a small quantity of cold water in another test-tube. Larger quantities of the gas may be made in a Florence flask. The fluid product is the *Acidum Sulphurosum*, B.P. It contains, if fairly saturated, about 6½ (6·4) per cent. of sulphurous acid (H_2SO_3), or about 5 per cent. of gas (SO_2). The process is also that described in the Pharmacopœia, except that the gas is purified by passing through a small wash-bottle before the final collection.

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{4H_2SO_4} + \underset{\substack{\text{Carbon}\\\text{(charcoal).}}}{C_2} = \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{2CO_2} + \underset{\text{Water.}}{4H_2O} + \underset{\substack{\text{Sulphurous}\\\text{acid gas.}}}{4SO_2}$$

Sulphurous acid gas may also be made by boiling copper, mercury, or iron with sulphuric acid, sulphate of the metal being formed. Also by boiling sulphur with sulphuric acid. The gas passed into water forms sulphurous acid.

$$\underset{\text{Sulphurous acid gas.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

If in this process the water were replaced by solutions of, or solid, metallic oxides or carbonates, sulphites of the various metals would be formed. The formula of Sulphite of Sodium (*Sodii Sulphis*, B.P., the old Sulphite of Soda) is Na_2SO_3, $7H_2O$; it occurs in colourless efflorescent prisms, soluble in water or spirit: under the name of *antichlor* it is used for removing traces of chlorine from paper pulp. The formula of Bisulphite of Sodium is $NaHSO_3$. The so-called *Bisulphite of Lime*, used by brewers for retarding or arresting fermentation and oxidation, and employed for various antiseptic purposes, is a solution of sulphite of calcium ($CaSO_3$) in free sulphurous acid (H_2SO_3), and is made by passing sulphurous acid gas (SO_2) into thin milk of lime. Its specific gravity varies from 1·050 to 1·070, and its potential strength of anhydride (SO_2) from 4 to 6 per cent. Sulphurous acid is very soluble in alcohol.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To a sulphite (of sodium, for instance,—made by passing sulphurous acid gas into solution of carbonate of sodium) add a drop or two of diluted hydrochloric acid; a well-known peculiarly pungent smell results (sulphurous acid).

This smell is the same as that evolved on burning lucifer matches that have been tipped with sulphur. It is due, probably not to the gas (SO_2), but to the sulphurous acid (H_2SO_3) formed by the union of sulphurous acid gas with either the moisture of the air or that on the surface of the mucous membrane of the nose. The gas is highly suffocating.

Second Analytical Reaction.—To a sulphite add a little water, a fragment or two of zinc, and then hydrochloric acid; sulphuretted hydrogen will be evolved, known by its odour and by its action on a piece of paper placed like a cap on the mouth of the test-tube and moistened with a drop of solution of acetate of lead, black sulphide of lead being formed. Sulphurous acid may be detected in acetic acid, or in hydrochloric acid, by this test:—$H_2SO_3 + 6H = H_2S + 3H_2O$.

Other Analytical Reactions.

To solutions of neutral sulphites add nitrate or chloride of barium, chloride of calcium, or nitrate of silver; in each case white precipitates result (sulphites of the various metals). The barium sulphite is soluble in weak hydrochloric acid; but if a drop or two of chlorine-water is first added, barium sulphate is formed, which is insoluble in acids. The other precipitates are also soluble in acids. The silver sulphite is decomposed on boiling, sulphuric acid being formed, and metallic silver set free, the mixture darkening in colour.

To recognise the three radicals in an aqueous solution of sulphides, sulphites, and sulphates, add chloride of barium, filter, and wash the precipitate. In the filtrate, sulphides are detected by the sulphuretted hydrogen evolved on adding an acid. In the precipitate, sulphites are detected by the odour of sulphurous acid, produced on adding hydrochloric acid, and sulphates by their insolubility in the acid.

QUESTIONS AND EXERCISES.

What are the differences between sulphurous acid and sulphurous acid gas, sulphites and acid sulphites?—State the characters of sulphurous acid gas.—How is the official sulphurous acid prepared?—By what tests may sulphurous acid be recognised in acetic acid?—Give a method by which sulphites may be detected in presence of sulphides and sulphates.

SULPHURIC ACID AND OTHER SULPHATES.

Formula of the Acid, H_2SO_4 or $SO_2(OH)_2$. Molecular weight, 98.

Many sulphates occur in nature; but the common and highly important hydrogen sulphate, sulphuric acid, is made artificially.

Preparation of the acid. General nature of the process.—Sulphur itself, or generally the sulphur in iron pyrites, is first converted into sulphurous acid gas by burning in air, and this gas, by moisture and oxygen, into sulphuric acid ($SO_2 + H_2O + O = H_2SO_4$).

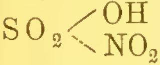
Details of the process.—The oxygen necessary to oxidize the sulphurous acid gas cannot directly be obtained from air, but indirectly, the agency of nitric oxide (NO), and nitrous anhydride (N_2O_3), being employed—these gases becoming nitric peroxide (NO_2) by action of the air, and the nitric peroxide again becoming reduced by the action of the sulphurous acid gas, and so on. A comparatively small quantity of nitric gases will thus act as carrier of oxygen from the air to very large quantities of sulphurous acid.

The nitric oxide and nitrous anhydride are in the first instance obtained from nitric acid, and this from nitrate of sodium by the action of a small quantity of the sulphuric acid of a previous operation.

The following equations represent the chief successive steps:—

$$\begin{gathered}
2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3 \\
2H_2O + 3SO_2 + 2HNO_3 = 3H_2SO_4 + 2NO \\
2SO_2 + H_2O + 2HNO_3 = 2H_2SO_4 + N_2O_3 \\
2NO + O_2 = 2NO_2 \quad | \quad N_2O_3 + O = 2NO_2 \\
2SO_2 + 2NO_2 + 2H_2O = 2H_2SO_4 + 2NO
\end{gathered}$$

Possibly the nitrous anhydride may, instead of absorbing oxygen, yield oxygen, and become reduced to nitric oxide, or may act in both ways. Probably also *nitrosulphonic acid*



$SO_2 \begin{matrix} \diagup OH \\ \diagdown NO_2 \end{matrix}$ is formed both from nitrous anhydride and nitric peroxide, and is then resolved by the steam into sulphuric acid and the lower oxides. And so on, over and over again.

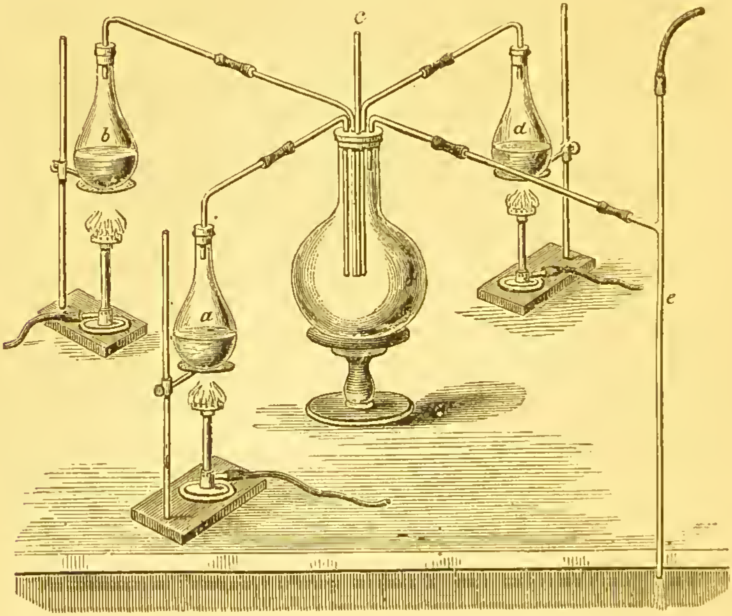
$$\begin{aligned}
2SO_2 + 3N_2O_3 + H_2O &= 2SO_2(OH)(NO_2) + 4NO \\
4SO_2 + 6NO_2 + 2H_2O &= 4SO_2(OH)(NO_2) + 2NO \\
2SO_2(OH)(NO_2) + H_2O &= 2H_2SO_4 + N_2O_3 \\
4SO_2(OH)(NO_2) + 2H_2O &= 4H_2SO_4 + 2NO_2 + 2NO
\end{aligned}$$

On the large scale, the sulphurous acid gas is carried, together with the nitric vapours, by flues into leaden chambers, where jets of steam supply the necessary moisture. The resulting dilute sulphuric acid is concentrated by evaporation in leaden, and finally in glass or platinum, vessels.

Other processes.—Sulphuric acid may be obtained by other processes, as by distilling the sulphate of iron resulting from the natural oxidation of iron pyrites by air; but it is not so made at the present day. The sulphate of iron was formerly called *green vitriol* (p. 161), and the distilled product *oil of vitriol;* the latter in allusion to its consistence and origin.

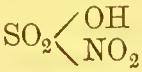
Experiment.—For purposes of practical study, a small quantity may be made, as shown in fig. 39, by passing, *a*, sulphurous acid gas (p. 358); *b*, nitric oxide in small quantity (p. 336); *c*, air (forced through by aid of bellows or a gas-holder, or drawn through by a *water-aspirator*, *e*); and, occasionally, *d*, steam (generated in a Florence flask), through glass tubes, nearly to the bottom of a two- or three-quart flask.

Fig. 39.



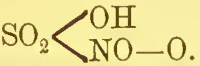
EXPERIMENTAL MANUFACTURE OF SULPHURIC ACID.

A slow current of sulphurous acid gas, air, and steam, and a small quantity of nitric oxide, will furnish, in the course of a few minutes, enough sulphuric acid for recognition by the first of the following analytical reactions. The manufacturing process may be more exactly imitated by burning sulphur in a tube placed where the flask *a* is represented in the foregoing figure, or by burning it under a funnel there attached; but in either case strong aspiration must be maintained. An instructive result, also, will follow the cessation of the steam-current for a short time, namely, the growth on the inner surface of the large flask of "chamber crystals," which are either nitro-sulphonic acid or nitrosyl-sulphuric acid:—



$SO_2\left\langle\begin{matrix}OH\\NO_2\end{matrix}\right.$

Nitro-sulphonic acid.



$SO_2\left\langle\begin{matrix}OH\\NO{-}O.\end{matrix}\right.$

Nitrosyl-sulphuric acid.

Purification.—Sulphuric acid may contain arsenic, nitrous-compounds, and salts (sulphate of lead, etc.). Arsenic may be detected by the hydrogen test (p. 195), or the stannous chloride test (p. 198), nitrous compounds by powdered sulphate of iron (which acquires a violet tint if they are present), and salts by the residue left on boiling a little to dryness in a crucible in a fume-chamber. If only nitrous compounds are present, the acid may be purified by heating with about half per cent. of sulphate of ammonium—water and nitrogen being produced (Pelouze). If arsenic occurs, heat with a little nitric acid (or nitrate of sodium), which converts arsenious anhydride (As_2O_3) into arsenic anhydride (As_2O_5), then add sulphate of ammonium, and distil in a retort containing pieces of quartz and heated by an annular-shaped burner (to prevent "bumping"—*see* page 326). This is the usual process of purification. The arsenic anhydride remains in the retort. (Arsenious anhydride would be carried over with the sulphuric acid vapours.) The distillation frees the acid from other salts (such as $NaHSO_4$) which are not volatile.

Quantivalence.—The sulphuric radical being bivalent (SO_4''), acid as well as neutral sulphates may exist. Acid sulphate of potassium ($KHSO_4$) is an illustration of the former, sulphate of sodium (Na_2SO_4) of the latter; *double sulphates* may also occur, such as that of potassium and magnesium ($K_2SO_4,MgSO_4,6H_2O$). Sulphates generally contain water of crystallization.

Pure sulphuric acid (H_2SO_4) is of specific gravity 1·848. The best "oil of vitriol" of commerce, a colourless liquid of oily consistence, is of specific gravity 1·843, and contains about 98 per cent. of real acid (H_2SO_4). This is the *Acidum Sulphuricum*, B.P. A variety less pure than this "white" acid is known as "brown acid." The *Acidum Sulphuricum*

Dilutum, B.P., sp. gr. 1·094, contains about 13½ (13·64) per cent. of acid (H_2SO_4) (the dilution commonly resulting in the separation, as a slight white sediment, of the sulphate of lead usually present in the strong acid); and the *Acidum Sulphuricum Aromaticum*, B.P., a dilute acid with which is mixed tincture of ginger and spirit of cinnamon, also contains about 13 per cent. of acid (H_2SO_4). It has been stated that in this preparation the acid and alcohol form some sulphovinic acid; but the author has been unable to detect the latter. There are some definite compounds of sulphuric acid with water; the first (H_2SO_4, H_2O) may be obtained in crystals.

Sulphuric anhydride (SO_3) occurs in white crystals having no acid properties. It may be made by distilling sulphuric acid with phosphoric anhydride ($H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$). On the large scale, sulphuric acid is dissociated by heat, and the dried sulphurous anhydride and oxygen made to recombine. It appears to unite with sulphuric acid and some other sulphates to form compounds (R'_2SO_4, SO_3) resembling in constitution red chromate or *pyrochromate* of potassium. The fuming sulphuric acid (H_2SO_4, SO_3), somotimes termed *pyrosulphuric acid* ($H_2S_2O_7$), formerly made at Nordhausen, in Saxony, seems to be such a body.

Note.—Sulphuric acid is a most valuable compound to all chemists and manufacturers of chemical substances. By its agency, direct or indirect, many, if not most, chemical transformations are effected. To describe all its uses would be to write a work on Chemistry.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To solution of a sulphate add solution of a barium salt; a white precipitato (sulphate of barium, $BaSO_4$) falls. Add nitric acid and boil tho mixturo, the precipitate does not dissolve.

This reaction is as highly characteristic of sulphates as it has been stated to be of barium salts (*vide* page 112). The only error likely to be made in its application is that of overlooking the fact that nitrate and chloride of barium are less soluble in strong acid than in water. On adding the barium salt to the acid liquid, therofore, a white precipitato may be obtained, which is simply the nitrate or chloride of barium. The appearance of such a precipitate differs considerably from that of the barium sulphate; hence a careful operator will not be misled. Should any doubt remain, water should be added, which will dissolve the nitrate or chloride, but not affect the sulphate.

Second Analytical Reaction.—Mix a fragment of an insoluble sulphate ($BaSO_4$, *e.g.*) with carbonate of potassium or of sodium, or, better, with both carbonates, and fuse the mixture in a small crucible. Digest the residue, when cold, in water, and filter; the filtrate may be tested for the sulphuric radical.

This is a convenient method of qualitatively analysing insoluble sulphates, such as those of barium and lead.

Third Analytical Reaction.—Mix a fragment of an insoluble sulphate with a little alkaline carbonate on a piece of charcoal, taking care that some of the charcoal dust is included in the mixture. Heat the little heap in the blowpipe-flame until it fuses, and, when cold, add a drop of acid; sulphuretted hydrogen is evolved, recognised by its odour.

This is another process for the recognition of insoluble sulphates. Other preparations of sulphur, and sulphur itself, give a similar result. It is therefore rather a test for sulphur and its compounds than sulphates only; but the absence of other salts can be determined previously.

Note.—The presence of the sulphuric radical in a solution having been proved by the above reactions, its occurrence as a neutral sulphate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper, and the detection of the metal; its occurrence as sulphuric acid or an acid sulphate by the sourness of the liquid to the taste, and the abundant effervescence produced on the addition of a carbonate.

Antidote.—In cases of poisoning by strong sulphuric acid, solution of carbonate of sodium (common washing soda), magnesia and water, etc., may be administered as antidotes.

QUESTIONS AND EXERCISES.

State the formula and molecular weight of sulphuric acid.—How is it related to other sulphates?—Write a short article on the manufacture of sulphuric acid, giving either diagrams or equations.—How may nitrous compounds be detected in, and eliminated from, sulphuric acid?—State the method for detecting arsenic in sulphuric acid, and explain the process by which it may be removed.—Define sulphates, acid sulphates, and double sulphates.—What percentage of real acid is contained in oil of vitriol?—State the strength of "diluted" and "aromatic" sulphuric acid.—By what process is sulphuric anhydride obtained from the ordinary sulphuric acid?—Explain the reactions which occur in testing for sulphates.—Ascertain by calculation the weight of oil of vitriol (of 96·8 per cent.) necessary for the production of one ton of dry sulphate of ammonium. *Ans.*, 1,718 lbs.—Name the antidotes in cases of poisoning by strong sulphuric acid.

CARBONIC ACID AND OTHER CARBONATES.

Formula of the acid, H_2CO_3 or $CO(OH)_2$; molecular weight, 62. Formula of carbonic acid gas, or carbonic anhydride, commonly termed carbonic acid, CO_2; molecular weight, 44.

Sources.—Carbonates (compounds containing the grouping CO_3) are very common in nature, the calcium carbonate ($CaCO_3$) being widely distributed as chalk, limestone, or marble. The hydrogen carbonate, true carbonic acid, is not known, unless, indeed, carbonic acid gas assumes that condition on dissolving in water. Such a solution (see p. 91) changes the colour of blue litmus-paper, and the gas does not; this may be because only the true acid (H_2CO_3) affects the litmus, or because the gas (CO_2) cannot come into real contact with the litmus without a medium. From the commonest natural carbonate, carbonate of calcium, is derived the carbonic constituent of the one most frequently used in medicine and in the arts generally, carbonate of sodium.

Carbonate of sodium, the old Carbonate of Soda, is prepared from the chief natural salt, the chloride, by two different processes. The first is "the Leblanc process." After the chloride has been converted into sulphate (salt-cake) by sulphuric acid (or by sulphurous acid, air, and steam—Hargreave's modification), $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$, the sulphate is roasted with limestone and small coal, carbonate of sodium and sulphide of calcium being formed, $Na_2SO_4 + C_2 + CaCO_3 = CaS + Na_2CO_3 + 2CO_2$.

The residual mass (black-ash) is digested in water, in which the carbonate of sodium dissolves, the sulphide of calcium remaining insoluble. The solution is evaporated to dryness, and yields crude carbonate of sodium. This is roasted with a small quantity of sawdust, to convert any caustic soda, resulting from the action of the lime on the carbonate, into neutral carbonate. The product is *soda-ash.* Dissolved in water and crystallized, it constitutes the ordinary "soda" used for washing purposes: recrystallized and sometimes ground, it forms the official carbonate of sodium (*Sodii Carbonas*, B.P.) (Na_2CO_3, $10H_2O$). The reaction will be more intelligible if regarded as occurring in two stages:—1st, reduction of the sulphate of sodium to sulphide by the carbon of the coal, $Na_2SO_4 + C_2 = Na_2S + 2CO_2$; 2nd, reaction of the sulphide of sodium and carbonate of calcium, giving soluble carbonate of sodium, thus, $Na_2S + CaCO_3 = Na_2CO_3 + CaS$.

$$\underbrace{2NaCl + H_2SO_4 + CaCO_3 + C_2}_{\text{The raw materials.}} = \underbrace{Na_2CO_3 + CaS + 2HCl + 2CO_2}_{\text{The factory products.}}$$

The sulphur in the residual sulphide of calcium may be recovered by exposure to the action of the waste carbonic acid gas of lime-kilns, carbonate of calcium being formed, and the diluting nitrogen passing off, more carbonic acid afterwards causing sulphuretted hydrogen to be set free. The latter is either burnt and converted into sulphuric acid, or is caused to react with air on ferric oxide, sulphur being set free.

The other process is "the ammonia process," so-called because ammonia (NH_3) is used over and over again as the chief agent, or chemical tool, so to say, in the factory. Strong brine from salt beds is saturated first with ammonia gas (from coal which also yields gaseous fuel and coke) and then with carbonic acid gas (from coke-heated limestone). Bicarbonate of sodium falls as a precipitate, and is afterwards heated to furnish the carbonate of sodium—with simultaneous temporary recovery of part of the carbonic acid gas. The chloride of ammonium concurrently produced is, by the latest improvements, separated and heated and its vapours passed over magnesia, chloride of magnesium and regenerated ammonia gas resulting. Air passed over the heated chloride of magnesium furnishes chlorine and recovered magnesia. The chlorine passed over lime (from the limestone) furnishes chlorinated lime. The former part of this process was discovered by Dyar and Hemming in 1838, and was applied, chiefly by Solvay, from 1861 to 1872; the working out of the chlorine-recovery by the magnesia method is largely due to Mond. The following notes will aid the student. *a.* Coal yields ammonia gas, gaseous fuel and coke. *b.* $CaCO_3 = CaO + CO_2$. c. $2NaCl + 2NH_3 + 2CO_2 + 2H_2O = 2NaHCO_3 + 2NH_4Cl$. *d.* $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. *e.* $2NH_4Cl + MgO = MgCl_2 + 2NH_3 + H_2O$. *f.* $MgCl_2 + O = MgO + Cl_2$. *g.* $Cl_2 + CaO = CaOCl_2$. (If the chlorine-recovery is not practised, then $2NH_4Cl + CaO = 2NH_3 + CaCl_2$, the latter being lost.) Rarely is a process carried on with such economy of elements as here obtains, while the salt, limestone and fuel occur in England in close contiguity. After these raw materials, labour, wear and tear, loss, and capital, are all paid for, single 1-cwt. casks of powdered bicarbonate ($NaHCO_3$) or of *granular monohydrous carbonate* (Na_2CO_3,H_2O) can be supplied at one penny per pound.

$$\underset{\text{The raw materials.}}{2NaCl + CaCO_3 + O} \quad = \quad \underset{\text{The factory products.}}{Na_2CO_3 + CaOCl_2}$$

Carbonic acid gas (CO_2) is a product of the combustion of all carbonaceous matters. It is constantly exhaled by animals and inhaled by plants, its intermediate storehouse being the atmosphere, throughout which it is equally distributed by *diffusion* (*vide* p. 15) to the extent of about 4 parts in 10,000. A larger proportion than that just mentioned gives to confined air depressing effects, 4 or 5 per cent. rendering the atmosphere poisonous when taken into the blood from the lungs. Carbonic acid, however, may be taken into the stomach with beneficial sedative effects; hence, probably, much of the value of such effervescing liquids as soda-water, lemonade, and solutions of the various granulated preparations and effervescing powders. The gas liquefies on being compressed, and the liquid solidifies on being cooled. The weights of equal bulks of the gas, of air, and of hydrogen are as 22, 14·44, and 1. At common temperatures it dissolves in about its own volume of water, both being under the same pressure, the water retaining gas strongly if all air has been expelled.

Sulphocarbonates resemble carbonates in constitution, but contain sulphur in place of oxygen.

Sulphocarbonic anhydride, CS_2, commonly termed *disulphide* or *bisulphide of carbon* (*Carbonei Disulphidum*, U.S.P.), is a highly volatile and inflammable liquid, easily made from its elements. Sp. gr. 1·272 at 15° C.; boiling-point, 46° C. It may be rendered almost scentless by digestion with lime and then with copper turnings. Its possible impurities are dissolved sulphur, sulphur oils, and sulphuretted hydrogen. It is slightly soluble in water, about 1 in 400, forming a useful antiseptic fluid.

REACTIONS.

Synthetical and Analytical Reactions.—1. To a fragment of marble in a test-tube add water and then hydrochloric acid; carbonic acid gas (CO_2) is evolved, and may be conveyed into water or solutions of salts by the usual delivery-tube.

This is the process of the British Pharmacopœia, and the one usually adopted for experimental purposes. On the large scale, the gas is prepared from chalk or marble and sulphuric acid, frequent stirring promoting its escape.

2. Pass the gas into lime-water; a white precipitate of carbonate of calcium ($CaCO_3$) falls. Solution of subacetate of lead may be used instead of, and is perhaps even a more delicate test than, lime-water.

The evolution of a gas on adding an acid to a salt, warming the mixture if necessary, the gas being inodorous and giving a white precipitate with lime-water, is sufficient evidence of the presence of a carbonate. Carbonates in solutions of ammonia, potash, or soda may be detected by the direct addition of solution of lime. Carbonates in presence of sulphites or hyposulphites may be detected by adding acid tartrate of potassium, which decomposes carbonates with effervescence, but does not attack sulphites or hyposulphites.

3. Blow air from the lungs through a glass tube into lime-water; the presence of carbonic acid gas is at once indicated.

The passage of a considerable quantity of normal air through lime-water produces a similar effect. A bottle containing lime-water soon becomes coated with carbonate of calcium from absorption of atmospheric carbonic acid gas.

4. Fill a dry test-tube with the gas, by passing the delivery-tube of the above apparatus to the bottom of the test-tube. Being rather more than once and a half as heavy as the air (1·529), it will displace the latter. Prove the presence of the gas by pouring it slowly, as if a visible liquid, into another test-tube containing lime-water; the characteristic cloudiness and precipitate are obtained on gently shaking the lime-water.

In testing for carbonates by bringing evolved gas into contact with lime-water, the preparation and adaptation of a delivery-tube may often be avoided by pouring the gas from the generating-tube into that containing the lime-water in the manner just indicated.

5. Pass carbonic acid gas through lime-water until the precipitate at first formed is dissolved. The resulting liquid is a solution of carbonate of calcium in carbonic acid water. Boil the solution; carbonic acid gas escapes, and the carbonate is again precipitated.

This experiment will serve to show how chalk is kept in solution in ordinary well-waters, giving the property of "hardness," and how the *fur* or stone-like deposit in tea-kettles and boilers is formed. It should be here stated that sulphate of calcium produces similar hardness, and that these, with small quantities of the sulphate and carbonate of magnesium, constitute the hardening constituents of well-waters, a curd (oleate of calcium or magnesium) being formed whenever soap is used with such waters. An enormous amount of soap is wasted through the employment of hard water for washing purposes. The hardness produced by the earthy carbonates is termed "temporary hardness," because removable by ebullition; that by the earthy sulphates "permanent hardness," because unaffected by ebullition. The addition of lime-water, or a mixture of lime and water, removes temporary hardness (Reaction 2, page 369), and carbonate of sodium, "washing-soda," both temporary and permanent hardness, in the latter case sulphate of sodium remaining in solution. Carbonate of barium (ground witherite) also decomposes sulphates of calcium and magnesium, sulphate of barium being precipitated and carbonates of calcium or magnesium formed; the latter and the carbonates originally in the water may then be precipitated by ebullition or by the action of lime-water. But the injurious effects of barium salts on man and the lower animals prevents the carbonate being used for purifying water for drinking purposes, as by accident or an unforeseen reaction a portion might become dissolved.

6. Add a solution of *carbonate* of potassium or of sodium to a mercuric salt; a brownish-red precipitate results. Add a solution of *bicarbonate* of potassium or of sodium to a mercuric solution; a white precipitate results, becoming red after some time.

QUESTIONS AND EXERCISES.

Name the chief natural carbonates.—What are the formulæ of carbonic acid and carbonic acid gas?—Adduce evidence of the existence of true carbonic acid.—Trace the steps by which the carbonic constituent of chalk is transferred to sodium by the two processes usually adopted in alkali-works—the manufacture of "soda."—Carbonic acid gas is constantly exhaled from the lungs of animals; why does it not accumulate in the atmosphere?—What is the effect of pressure on carbonic acid gas?—State the specific gravity of carbonic acid gas.—By what process may carbonic acid gas be obtained for experimental and manufacturing purposes?—Describe the action of carbonic acid gas on the carbonate of potassium or of sodium.—How may carbonic acid gas be detected in expired air?—To what extent is carbonic acid gas heavier than air?—Work sums showing what quantity of chalk (90 per cent. pure) will be required to furnish the carbonic acid gas necessary to convert one ton of carbonate of potassium (containing 83 per cent. of K_2CO_3) into acid carbonate, supposing no gas to be wasted. *Ans.*, 1,500 lbs.—Define "hardness" in water.—How may the presence of carbonates be demonstrated?

OXALIC ACID AND OTHER OXALATES.

Formula of Oxalic Acid, $H_2C_2O_4$, $2H_2O$, or $(COOH)_2$, $2H_2O$.
Molecular weight, 126.

Sources.—Oxalates occur in nature in the juices of some plants, as wood-sorrel, rhubarb, the common dock, and certain lichens; but the hydrogen oxalate (oxalic acid) and other oxalates are all made artificially. The carbon of many organic substances yields oxalic acid when those substances are boiled with nitric acid, and an alkaline oxalate when they are roasted with a mixture of the hydrates of potassium and sodium.

Experimental process.—On the small scale, a mixture of nitric acid 10 parts, loaf-sugar 2 parts, and water 3 parts, quickly yields the acid. Abundance of red fumes are at first evolved. On cooling, crystals are deposited. A more dilute acid, kept warm, acts more slowly but yields a larger product. The following process is more economical.

Manufacturing process.—On the large scale, sawdust is roasted with alkalies, resulting oxalate of sodium decomposed by lime, with regeneration of the soda, and formation of oxalate of calcium, the latter digested with sulphuric acid, and the liberated oxalic acid (Oxalic Acid of Commerce, B.P.) made commercially pure by recrystallization.

Purified oxalic acid.—The acid made from sugar, recrystallized two or three times, is quite pure. Commercial acid should be mixed with insufficient water for complete solution, and the mixture occasionally shaken. Most of the impurities remain undissolved, and the saturated aqueous solution evaporated yields crystals which are fairly pure.

Quantivalence.—The elements represented by the formula C_2O_4 are those characteristic of oxalates. They form a bivalent grouping; hence neutral oxalates ($R'_2C_2O_4$) and acid oxalates ($R'HC_2O_4$) exist.

Salt of sorrel is a crystalline compound of oxalic acid with acid potassium oxalate, the crystals containing two molecules of water of crystallization (KHC_2O_4, $H_2C_2O_4$, $2H_2O$).

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of an oxalate (oxalate of ammonium, *e.g.*) add solution of chloride of calcium; a white precipitate falls (oxalate of calcium, CaC_2O_4). Add to the precipitate excess of acetic acid; it is insoluble. Add hydrochloric acid; the precipitate is dissolved.

The formation of a white precipitate on adding a calcium or barium salt, insoluble in acetic but soluble in hydrochloric or nitric acid, is usually sufficient proof of the presence of an oxalate. The action of the liquid on litmus-paper, effervescence with carbonate of sodium, and absence of metals, would indicate that the oxalate is that of hydrogen, oxalic acid.

Note.—The *barium* oxalate *is* slightly soluble in acetic acid (Souchay and Lenssen), and enough may be dissolved by this acid from a mixed barium precipitate (produced on adding chloride or nitrate of barium to a solution of mixed salts) to give the foregoing reaction on adding chloride of calcium to the filtered acetic liquid—an effect sometimes useful in the analysis of mixed substances (Davies).

Antidote.—In cases of poisoning by oxalic acid or salt of sorrel, chalk and water may be administered as a chemical antidote (with the view of producing the insoluble oxalate of calcium), emetics and the stomach-pump, or stomach-siphon, being used as soon as possible.

Second Analytical Reaction.—Heat a fragment of any dry common fixed metallic oxalate (an oxalate of potassium, for example) in a test-tube; decomposition occurs, carbonic oxide (CO) (a gas that will be noticed subsequently) is liberated, and a carbonate of the metal remains. Add water and then an acid to the residue; effervescence occurs.

This is a ready test for ordinary insoluble oxalates, and is trustworthy if, on heating the substance, no charring occurs, or not more than gives a grey colour to the residue. Organic salts of metals decompose when heated, and leave a residue of carbonate, but, except in the case of oxalates, the residue is always accompanied by much charcoal. Insoluble oxalates and organic salts of such metals as lead and silver are, of course, liable to be reduced to oxide or even metal by heat. Such oxalates may be decomposed by boiling with solution of carbonate of sodium, filtering and testing the filtrate for oxalates by the chloride of calcium test.

Other Analytical Reactions.—Nitrate of silver gives, with oxalates, a white precipitate (oxalate of silver, $Ag_2C_2O_4$). ——Dry oxalates are decomposed when heated with strong sulphuric acid, carbonic oxide and carbonic acid gases escaping. If much of the substance be operated on, the gas may be washed with an alkali, the carbonic acid be thus removed, and the carbonic oxide be ignited; it will be found to burn with a characteristic bluish flame. —— Oxalates, when mixed with water, black oxide of manganese (free from carbonates), and sulphuric acid, yield carbonic acid gas, which may be tested by lime-water in the usual manner.——Not only such insoluble oxalates as those of lead and silver above referred to, but any common insoluble oxalate, such as that of calcium or magnesium, may be decomposed by ebullition with solution of carbonate of sodium; after filtration the oxalic radical will be found in the clear liquid as soluble oxalate of sodium.

QUESTIONS AND EXERCISES.

Explain the constitution of oxalates.—State how oxalates are obtained.—What is the quantivalence of the oxalic radical?—Give the formula of "salt of sorrel."—Mention the chief test for oxalic acid and other soluble oxalates.—Name the antidote for oxalic acid, and describe its action.—By what reactions are insoluble oxalates recognised?

TARTARIC ACID AND OTHER TARTRATES.

Formula of Tartaric Acid, $H_2C_4H_4O_6$ or $C_2H_2(OH)_2(COOH)_2$.
Molecular weight, 150.

Sources.—Tartrates exist in the juice of many fruits; but it is from that of the grape that our supplies are usually obtained. Grape-juice contains much acid tartrate of potassium ($KHC_4H_4O_6$), which is gradually deposited when the juice is fermented, as in making wine; for acid tartrate of potassium, not very soluble in aqueous liquids, is still less so in spirituous, and hence crystallizes out as the sugar of the grape-juice is gradually converted into alcohol. It is found, with tartrate of calcium, lining the vessels in which wine is kept; and it is from this crude substance, termed *argal* or *argol*, also from the albuminoid yeasty matter or "lees" deposited at the same time, as well as from what tartrate may be remaining in the marc left after the juice has been pressed from the grapes, that by rough recrystallization "tartar," still containing 6 or 7 per cent. or more of anhydrous tartrate of calcium ($CaC_4H_4O_6$), is obtained. From the tartar, tartaric acid and other tartrates are prepared. In old dried grapes (Raisins; *Uvæ*, B.P.) crystalline masses of tartar and of grape-sugar are constantly met with.

Cream of tartar, purified by crystallization (*Potassii Tartras Acida*, B.P.), occurs as " a gritty white powder, or fragments of cakes crystallized on one surface;" of a pleasant acid taste, soluble in 180 parts of cold and 6 of boiling water, insoluble in spirit.*

Quantivalence.—The elements represented by the formula $C_4H_4O_6$ are those characteristic of tartrates. They form a bivalent grouping; hence neutral tartrates ($R'_2C_4H_4O_6$) and acid tartrates ($R'HC_4H_4O_6$) exist. Tartrate of potassium, the *Potassii Tartras* of the British Pharmacopœia ($K_2C_4H_4O_6$), and Rochelle Salt, or tartrate of potassium and sodium, the official *Soda Tartarata*, are illustrations of neutral tartrates, while Cream of Tartar, $KHC_4H_4O_6$, is an example of acid tartrates. The only official tartrate not apparently included in these general formulæ is tartar-emetic (*Antimonium Tartaratum*, B.P.), which is sometimes regarded as the double tartrate of potassium and a hypothetical radical, antimonyl (SbO), thus, $KSbOC_4H_4O_6$. Probably, however, it is but an oxytartrate of antimony ($Sb_2O_2C_4H_4O_6$) with normal tartrate of potassium ($K_2C_4H_4O_6$); for there are several oxycompounds of antimony analogous to the oxycompounds of bismuth that have been described (p. 293), normal salts partially decomposed by water into oxides, and many of these oxycompounds readily unite with normal salts of other basylous radicals. Tartar-emetic would thus be oxytartrate of antimony with tartrate of potassium [$Sb_2O_2C_4H_4O_6,K_2C_4H_4O_6$, or $K'Sb'''(C_4H_4O_6)''O''$].

Tartaric Acid.

Tartaric Acid (*Acidum Tartaricum*, B.P.) is obtained, according to the British Pharmacopœia, by boiling cream of tartar (*Potassii Tartras Acida*, B.P.) with water, adding chalk till effervescence ceases, and then chloride of calcium so long as a precipitate falls; the two portions of tartrate of calcium thus consecutively formed are thoroughly washed, treated with sulphuric acid, the mixture boiled for a short time, resulting sulphate of calcium mostly separated by filtration, the filtrate concentrated by evaporation, any sulphate of calcium that may have deposited removed as before, and concentration continued until the solution is strong enough to crystallize. Tartrate of calcium from nine ounces of cream of tartar requires five ounces by weight of sulphuric acid for complete decomposition.

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* A boiling solution of tartar yields a floating crust of minute crystals on cooling—just as milk yields a floating layer of cream; hence the term *cream* of tartar. " It is called *tartar*," says Paracelsus, " because it produces oil, water, tincture, and salt, which burn the patient as tartarus does." *Tartarus* is Latin (Τάρταρος, Tartaros, Greek) for *hell*. The products of its destructive distillation are certainly somewhat irritating in taste and smell; and the " salt " (carbonate of potassium) that is left is diuretic and in larger quantities powerfully corrosive.

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Carbonate of calcium.}}{CaCO_3} = \underset{\text{Tartrate of calcium.}}{CaC_4H_4O_6} + \underset{\text{Tartrate of potassium.}}{K_2C_4H_3O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

$$\underset{\text{Tartrate of potassium.}}{K_2C_4H_4O_6} + \underset{\text{Chloride of calcium.}}{CaCl_2} = \underset{\text{Tartrate of calcium.}}{CaC_4H_4O_6} + \underset{\text{Chloride of potassium.}}{2KCl}$$

$$\underset{\text{Tartrate of calcium.}}{2CaC_4H_4O_6} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Sulphate of calcium.}}{2CaSO_4} + \underset{\text{Tartaric acid.}}{2H_2C_4H_4O_6}$$

Tartaric acid occurs in trade as colourless crystals, or the same powdered. It is strongly acid and readily soluble in water or spirit. One part in eight of water and two of spirit of wine forms "Solution of Tartaric Acid," B.P. Its aqueous solution is not stable.

Parcels of tartaric acid often contain crystals of an allotropic or physically isomeric modification (*vide* "Allotropy" and "Isomerism" in Index). It is termed *Paratartaric acid* (παρὰ, *para*, beside) or *Racemic acid* (*racemus*, a bunch of grapes), and is a combination of ordinary tartaric acid, whose solution twists a ray of polarized light to the right hand (dextrotartaric or dextroracemic acid), and of lævotartaric or lævoracemic acid, whose solution twists a polarized ray to the left.* Racemic acid is inactive in this respect, the opposite properties of its constituents neutralizing each other. Racemic acid is less soluble in alcohol than tartaric acid.

REACTIONS.

Tartrate of Potassium.

Synthetical Reactions.—To a small quantity of a strong solution of carbonate of potassium add acid tartrate of potassium, so long as effervescence occurs; the resulting liquid is solution of neutral tartrate of potassium (*Potassii Tartras*, B.P.) ($K_2C_4H_4O_6$), crystals of which may be obtained on evaporation.

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* According to Van 't Hoff and Le Bel, all compounds that cause such rotation contain at least one atom of carbon with which is united four *different* atoms or radicals. Such carbon atoms are conveniently termed *asymmetrical*.

Note.—This is a common method of converting an acid salt of a bivalent acidulous radical into a neutral salt. The carbonate added need not be a carbonate of the same, but may be of a different metal; compounds like Rochelle salt ($KNaC_4H_4O_6$) are then obtained. Thus:—

Tartrate of Potassium and Sodium.

To a strong hot solution of carbonate of sodium add acid tartrate of potassium until effervescence ceases; the resulting liquid is solution of tartrate of potassium and sodium: on cooling, it yields crystals. This is the official process (*Soda Tartarata*, B.P.) ($KNaC_4H_4O_6$, $4H_2O$).

$$\begin{array}{ccccccccc} Na_2CO_3 & + & 2KHC_4H_4O_6 & = & 2KNaC_4H_4O_6 & + & H_2O & + & CO_2 \\ \text{Carbonate of} & & \text{Acid tartrate} & & \text{Tartrate of potas-} & & \text{Water.} & & \text{Carbonic} \\ \text{sodium.} & & \text{of potassium.} & & \text{sium and sodium.} & & & & \text{acid gas.} \end{array}$$

Crystals of Rochelle salt are usually halves of colourless transparent right rhombic prisms, slightly efflorescent in dry air, soluble in five parts of boiling water. Tartrate of potassium is slightly deliquescent, soluble in about four parts of boiling water.

Equivalent Weights *of Tartaric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium* (*crystallized*), *Bicarbonate of Sodium and Carbonates of Ammonium and Magnesium: repeated for* 20 *parts of each* (and, incidentally for other proportions).

Tart. Acid .	$H_2C_4H_4O_6$ . . . . . . =150	**20**	**18¼**	**15**	**10½**	**17¾**	**28½**	**31½**
Carb. Potas..	K_2CO_3 (of 84 per cent.) . =164	**22**	**20**	16½	11½	19½	31½	34½
Bicarb. Pot..	$2(KHCO_3)$ . . . . . . =200	**26¾**	24¼	**20**	14	23¾	38¼	42
Carb. Sod. .	Na_2CO_3, $10H_2O$ . . . . =286	**38**	34¾	28½	**20**	34	54½	60
Bicarb. Sod.	$2(NaHCO_3)$ . . . . . =168	**22½**	20¼	16¾	11¾	**20**	32	35¼
Carb. Ammon.	$(N_3H_{11}C_2O_5) \div 3 \times 2$ . . =105	**14**	12¾	10½	7¼	12½	**20**	21¾
Carb. Magnes.	$(MgCO_3)_3Mg2HO$, $4H_2O \div 4$ =95·5	**12¾**	11½	9¾	6¾	11¼	18¼	**20**

Thus 20 parts (grains or other weights) of tartaric acid neutralize 22 of carbonate of potassium, 26¾ of bicarbonate of potassium, 38 of carbonate of sodium, 22½ of bicarbonate of sodium, 14 of carbonate of ammonium, or 12¾ of carbonate of magnesium. Other quantities of tartaric acid (**18¼, 15, 10½, 17¾, 28½, 31½**) saturate the amount of salts mentioned in the other columns, and *vice versâ*. A similar Table for Citric Acid will be found at p. 383, and for both acids in the Appendix. These Tables afford good illustrations of both of the laws of chemical combination (pp. 44, 225). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

Effervescent Tartarated Soda Powder (*Pulvis Sodæ Tartaratæ Effervescens*, B.P.) or *Seidlitz Powder* consists of 3 parts of Rochelle salt (120 grains) with 1 part (40 grains) of acid carbonate of sodium (the mixture usually wrapped in blue paper) and 1 part (38 grains) of tartaric acid (wrapped in white paper). When administered, one powder is dissolved in a tumbler rather more than half full of water, the other added, and the mixture drunk during effervescence. It will be seen that the salts swallowed are tartrate of potassium and sodium ($KNaC_4H_4O_6$, $4H_2O$), tartrate of sodium ($Na_2C_4H_4O_6$, $2H_2O$), and acid tartrate of sodium or of potassium. The last-mentioned salt results because, for one reason, 2½ grains of the tartaric acid is in excess of the quantity necessary for the formation of neutral tartrate of sodium; and, for another reason, because while carbonic acid remains in great excess, a neutral tartrate containing potassium may be converted more or less into acid tartrate of potassium and a bicarbonate. This amount of acid salt gives, according to the taste of some persons, agreeable acidity to the draught. The American formula (*Pulvis Effervescens Compositus*, U.S.P.) includes rather less tartaric acid, so that only neutral salts are formed, and the occurrence, or permanent occurrence of the gritty acid tartrate of potassium avoided. "Double" seidlitz powders contain a double dose of Rochelle salt.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To solution of any normal tartrate, or tartaric acid made neutral by solution of soda, add solution of chloride of calcium ; a white precipitate (tartrate of calcium, $CaC_4H_4O_6, 4H_2O$) falls. Collect the precipitate on a filter, wash, place a small quantity in a test-tube, and add solution of potash : on stirring the mixture the precipitate dissolves. Heat the solution : the tartrate of calcium is again precipitated.

In this reaction a fair amount of the chloride of calcium solution should be added at once, and the test be performed without delay, or the calcium tartrate will assume a crystalline character, and be with difficulty dissolved by the potash. The potash should be quite free from carbonate.

The solubility of tartrate of calcium in cold potash solution enables the analyst to distinguish between tartrates and citrates, otherwise a difficult matter. Citrate of calcium is not soluble, or only to a very slight extent, in the alkali. The absence of much ammoniacal salt must be ensured, citrate, as well as tartrate, of calcium being soluble in solutions of salts of ammonium.

Second Analytical Reaction.—Acidulate a solution of a tartrate with acetic acid, add acetate of potassium, and well stir the mixture ; a crystalline precipitate (acid tartrate of potassium) slowly separates.

This reaction is not applicable in testing for very small quantities of tartrates, the acid tartrate of potassium being not altogether insoluble. The precipitate being insoluble in alcohol, however, the addition of spirit of wine renders the test far more delicate.

Third Analytical Reaction.—To a neutral solution of a tartrate add solution of nitrate of silver ; a white precipitate (tartrate of silver, $Ag_2C_4H_4O_6$) falls. Boil the mixture ; it blackens owing to the reduction of the salt to metallic silver. Or, before boiling, add a drop, or less, of ammonia ; a mirror will form on the tube—adhering well to the glass if the tube was thoroughly cleansed. Even an insoluble tartrate, placed in a dry tube with a few fragments of nitrate of silver and a drop, or less, of ammonia added, gives a mirror-like character to each fragment of silver salt when the tube is gently rotated some inches above a flame.

Other Reactions.—Tartrates heated with strong sulphuric acid char immediately.——Tartaric acid and the soluble tartrates prevent the precipitation of ferric and other hydrates by alkalies, solutions of double tartrates being formed (which on evaporation yield liquids that do not crystallize, but, spread on sheets of glass, dry up to thin transparent plates or scales). The potassio-tartrate of iron (*Ferrum Tartaratum*, B.P.) is a preparation of this kind.——Tartrates decompose when heated, carbonates being formed and carbon set free, the gaseous products having a peculiar, more or less characteristic smell, resembling that of burnt sugar.

QUESTIONS AND EXERCISES.

State the origin of tartaric acid and other tartrates, and explain the deposition of argol, crude acid tartrate of potassium, during the manufacture of wine.—What is the chemical formula, and what are the characters, of "cream of tartar"?—Mention the formula and quantivalence of the tartaric radical.—Write formulæ of various tartrates, including tartar emetic.—Give equations or diagrams illustrative of the production of tartaric acid from cream of tartar.—By what general process may normal or double tartrates be obtained from acid tartrate of potassium?—Work out sums proving the correctness of some of the figures given on p. 377 as showing the saturating power of tartaric acid for various quantities of different carbonates, and give diagrams or equations of the reactions.—State the names and work sums showing quantities of the salts resulting from the admixture of 120 grains of tartrate of potassium and sodium, 40 grains of acid carbonate of sodium, and 38 grains of tartaric acid (seidlitz powder).—Enumerate the tests for tartrates, and explain the effects of heat on tartrates of the metals.

CITRIC ACID AND OTHER CITRATES.

Formula of Citric Acid, $H_3C_6H_5O_7$, H_2O.
Molecular weight, 210.

Source.—Citric acid (*Acidum Citricum*, B.P.) exists in the juice of the gooseberry, currant, cherry, strawberry, raspberry, and many other fruits, as well as in other parts of plants. The pulp of the fruit of *Tamarindus indica* (*Tamarindus*, B.P.) contains from 1 to 12 per cent. (in addition to 1·5 of tartaric acid, ·5 of malic acid, and 3 per cent. of acid tartrate of potassium). But it is from the lemon or lime that the acid of commerce is usually obtained. For this purpose concentrated lemon-juice is exported from Sicily, concentrated bergamot-juice from the Calabrian coast of South Italy, and concentrated lime-juice from the West Indies. The lime-fruit from *Citrus bergamia* is official in the Pharmacopœia of India.

Process.—The British Pharmacopœia directs that the hot lemon-juice (4 pints) be saturated by powdered chalk, that is, whiting ($4\frac{1}{2}$ ounces), the resulting citrate of calcium collected on a filter, washed with hot water till the liquor passes from it colourless (by which not only the colouring-matter, but the mucilage, sugar, and other constituents of the juice are got rid of), then mixed with cold water (1 pint), decomposed by sulphuric acid ($2\frac{1}{2}$ fluid ounces in $1\frac{1}{2}$ pints of water), the mixture boiled for half an hour, filtered, the solution evaporated to a density of 1·21, set aside for 24 hours, then poured off from any deposit of crystalline sulphate of calcium, further concentrated and set aside to crystallize. If the quantity of citrate of calcium to be decomposed is indefinite, the sulphuric acid may be added until a little of the supernatant fluid gives, after a minute or two, a precipitate with solution of chloride of calcium. The concentrated citric solution generally crystallizes very slowly. Shaken violently, however, in a bottle with a granule or two of solid acid, it quickly yields its citric acid in a pulverulent form, and this drained and redissolved in a very small quantity of hot water yields crystals fairly quickly (Warington).

$$\underset{\substack{\text{Citric acid}\\\text{(impure).}}}{2H_3C_6H_5O_7} + \underset{\substack{\text{Carbonate}\\\text{of calcium.}}}{3CaCO_3} = \underset{\substack{\text{Citrate of}\\\text{calcium.}}}{Ca_32C_6H_5O_7} + \underset{\text{Water.}}{3H_2O} + \underset{\substack{\text{Carbonic}\\\text{acid gas.}}}{3CO_2}$$

$$\underset{\substack{\text{Citrate of}\\\text{calcium.}}}{Ca_32C_6H_5O_7} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Citric acid}\\\text{(pure).}}}{2H_3C_6H_5O_7} + \underset{\substack{\text{Sulphate of}\\\text{calcium.}}}{3CaSO_4}$$

Quantivalence.—The elements represented by the formula $C_6H_5O_7$ are those characteristic of citrates. They form a trivalent grouping; hence three classes of salts may exist—

one, two, or three atoms of the basylous hydrogen in one molecule of the acid, $H_3C_6H_5O_7$, being displaced by equivalent proportions of other basylous radicals. Constitutional formula, $C_3H_4(OH)(COOH)_3$.

Citric acid itself is the only citric compound of much direct importance to the pharmacist. It usually occurs in colourless crystals soluble in half their weight of boiling and three-fourths of cold water, less soluble in spirit, and insoluble in ether. A solution of 36 to 46 grains in 1 ounce of water forms a sort of artificial lemon-juice. Citrates heated with strong sulphuric acid to about 215° F. evolve carbonic oxide gas, and at higher temperatures acetone and carbonic acid gas.

The artificial production of citric acid has been accomplished by Grimaux and Adam, who, starting with glycerine, produce certain chloro- and cyano-derivatives and ultimately citric acid itself.

Action of heat on citric acid.—Citric acid slowly heated first loses its water of crystallization; afterwards (347° F.) the elements of another molecule of water are evolved and a residue obtained from which ether extracts *aconitic acid*, $H_3C_6H_3O_6$, identical with the aconitic acid (and the acid first termed *equisetic*) in various species of *Aconitum* and *Equisetum*.

The official Lemon-juice (*Limonis Succus*, B.P.) is to be freshly expressed from the ripe fruit, have a specific gravity of 1·035 to 1·045, and contain 36 to 46 grains of citric acid ($H_3C_6H_5O_7$, H_2O) in 1 fluid ounce. The acidity may be ascertained by adding solution of potash or soda (the strength of which has been determined previously with pure crystals of citric acid) till red litmus-paper is fairly turned blue. Before applying this test to commercial specimens of lemon-juice, the absence of notable quantities of sulphuric, hydrochloric, acetic, tartaric, or other acid must be ensured by application of appropriate reagents. (*See* also "Lemon-juice" in Index.)

Lime-juice as imported into England contains an average of 7·84 per cent. of citric acid, rarely rising to 10 per cent. and very seldom falling to 7 per cent. Containing but little sugar and mucilage, it requires no addition of spirit to preserve it. *Lemon-juice* requires about 40 per cent. of proof spirit to prevent fermentation (Conroy).

Equivalent Weights *of Citric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium (crystallized), Bicarbonate of Sodium, and Carbonates of Ammonium and Magnesium: repeated for* 20 *parts of each* (and, incidentally, for other proportions).

Citric Acid	$H_3C_6H_5O_7,H_2O$ . . . . . $=210$	20	17	14	$9\frac{3}{4}$	$16\frac{3}{4}$	$26\frac{3}{4}$	$29\frac{3}{4}$
Carb. Pot. .	$(K_2CO_3$; of 84 per cent.$)\div 2 \times 3=246\frac{1}{2}$	$23\frac{1}{2}$	20	$16\frac{1}{2}$	$11\frac{1}{2}$	$19\frac{3}{4}$	$31\frac{1}{2}$	$34\frac{1}{4}$
Bicarb. Pot.	$3(KHCO_3)$ . . . . $=300$	$28\frac{1}{2}$	$24\frac{1}{4}$	20	14	23	$38\frac{3}{4}$	$41\frac{3}{4}$
Carb. Sod. .	$(Na_2CO_3; 10H_2O)\div 2\times 3$ . . $=429$	40	$34\frac{3}{4}$	$28\frac{1}{2}$	20	$34\frac{1}{4}$	$54\frac{1}{2}$	60
Bicarb. Sod.	$3(NaHCO_3)$ . . . . . . $=252$	24	$20\frac{1}{2}$	$16\frac{3}{4}$	$11\frac{3}{4}$	20	32	35
Carb. Amm.	$(N_3H_{11}C_2O_5)$ . . . . . . $=157$	15	$12\frac{3}{4}$	$10\frac{1}{2}$	$7\frac{1}{4}$	$12\frac{1}{2}$	20	$21\frac{3}{4}$
Carb. Mag.	$(MgCO_3)_3Mg2HO,4H_2O\div 8\times 3=143$	$13\frac{1}{2}$	$11\frac{3}{4}$	$9\frac{1}{2}$	$6\frac{3}{4}$	$11\frac{1}{2}$	$18\frac{1}{4}$	20

Thus 20 parts (grains, or other weights) of citric acid neutralize $23\frac{1}{2}$ of carbonate of potassium, $28\frac{1}{2}$ of bicarbonate of potassium, 40 of carbonate of sodium, 24 of bicarbonate of sodium, 15 of carbonate of ammonium, or $13\frac{1}{2}$ of carbonate of magnesium. Other quantities of citric acid (17, 14, $9\frac{3}{4}$, $16\frac{3}{4}$, $26\frac{3}{4}$, $29\frac{1}{4}$) saturate the amounts of salts mentioned in the other columns, and *vice versâ.*

This Table, the similar one for tartaric acid (p. 377), and that for both acids (*vide* Appendix) afford good illustrations of both of the laws of chemical combination (pp. 44, 225). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice, effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—To a dilute solution of any neutral citrate, or citric acid carefully neutralized by alkali, add solution of chloride of calcium and boil; a white precipitate (citrate of calcium, $Ca_32C_6H_5O_7$) falls. Treat the precipitate as for tartrate of calcium (p. 379); it is not perceptibly dissolved by the potash.

A mixture of citrates and tartrates can be separated by this reaction. They are precipitated as calcium salts, and the rapidly washed precipitate mixed with solution of potash, diluted and filtered; the filtrate contains the tartrate, which is shown to be present by reprecipitation on boiling. The precipitate still on the filter is washed, dissolved in solution of chloride of ammonium, and the solution boiled; the citrate of calcium is reprecipitated. The presence of much sugar interferes with this reaction. A dilute solution of a citrate is not precipitated by chloride of calcium until the liquid is heated: precipitation from a strong solution, also, is not thoroughly complete without ebullition of the mixture. This reaction is not thoroughly satisfactory, citrate of calcium being *slightly* soluble in alkalies, in the solutions of salts produced in the reaction, and, to a very slight extent, even in cold water. It is readily soluble in acetic acid.

Second Analytical Reaction.—To a *neutral* solution of a citrate add solution of nitrate of silver; a white precipitate (citrate of silver, $Ag_3C_6H_5O_7$) falls. Boil the mixture; the precipitate does not blacken as tartrate of silver does, or only after long boiling.

Other Analytical Reactions.—Citric acid forms no precipitate corresponding with the acid tartrate of potassium.—— Lime-water, in excess, gives no precipitate with citric acid or citrates, unless the solution is boiled, citrate of calcium being slightly soluble in cold but not in hot water; it usually precipitates tartrates in the cold.——Citrates, when heated with strong sulphuric acid, do not char immediately.——Citric acid and citrates prevent the usual precipitation of iron by alkalies, soluble double compounds being formed. The *Ferri et Ammonii Citras*, B.P., is a preparation of this kind.—— Metallic citrates decompose when heated, carbonates being formed and carbon set free; the odour of the gaseous products is not so characteristic as that of tartrates.——According to Cailletet a cold saturated solution of red chromate of potassium turns a solution of tartaric acid dark-brown, carbonic acid gas being evolved, while a solution of citric acid only slowly becomes of a light-brown.

Pusch's test for the detection of tartaric acid in citric acid depends on the well-known difference in the action of sulphuric acid on tartaric acid and on citric acid. It consists in adding to 1 gramme of powdered citric acid in a dry test-tube 10 grammes of strong pure (colourless) sulphuric acid, and keeping the part of the tube containing the mixture immersed in boiling water for an hour. The citric acid dissolves with evolution of gas and frothing to form a lemon-coloured liquid, and if the sample be pure this colour undergoes no change within half an hour; but if as much as half per cent. of tartaric acid be present, the lemon colour becomes brownish within that time, and in an hour the mixture is red-brown.

QUESTIONS AND EXERCISES.

What is the source of citric acid?—Describe the preparation of citric acid, giving diagrams.—Illustrate by formulæ the various classes of tartrates and citrates.—State the average proportion of citric acid in lemon-juice.—Work out sums proving the correctness of some of the figures given on p. 383 as showing the saturating power of citric acid for various carbonates.—What are the tests for citrates?—How are tartrates separated from citrates?

PHOSPHORIC ACID AND OTHER PHOSPHATES.

Formula of the Acid, H_3PO_4 or $PO(OH)_3$.
Molecular weight, 98.

Source.—The source of the ordinary normal phosphates and of phosphorus itself (*Phosphorus*, B.P.) is the normal phosphate of calcium (Ca_32PO_4). It is the chief constituent of the bones and teeth of animals, being derived from the plants on which they feed, plants again obtaining it from the soil. Compounds of phosphorus are also met with in the brain, nerves, muscles, blood, saliva, and, according to Kirkes, even in tissues so simple that one must assume that the compounds are necessary constituents of the substance of the primary cell. They escape from the system both in the urine and in the fæces.

Process.—Phosphorus ($P=31$) is obtained from bones by the following processes:—The bones are burnt to remove all traces of animal matter. The resulting *bone-earth* is treated with hot and fairly strong sulphuric acid, by which phosphoric acid and sulphate of calcium are produced :—

$$Ca_32PO_4 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4.$$

The acid fluid strained from the sulphate and concentrated, is mixed with charcoal, coke or sawdust, and dried in an iron pot. At this stage water escapes and metaphosphoric remains :—$2H_3PO_4 = 2HPO_3 + 2H_2O$.

The mixture is then transferred to a fireclay retort and strongly heated; phosphorus vapour is evolved and is condensed under water :—

$$4HPO_3 + C_{12} = H_2 + 12CO + P_4.$$

The phosphorus is purified by melting under water containing sulphuric acid and red chromate of potassium, and is filtered through canvas and cast into sticks.

Properties.—Phosphorus is "a semi-transparent, colourless, wax-like solid (in sticks or cakes), which emits white vapours when exposed to the air. Specific gravity, 1·77. It is soft and flexible at common temperatures, melts at 110° F., ignites in the air at a temperature a little above its melting-point, burning with a luminous flame and producing dense white fumes. It is very poisonous. Insoluble in water, but soluble in ether and in boiling oil of turpentine," also in bisulphide of carbon. It is soluble in oil which has been previously heated for a short time to about 300° F. to expel moisture—16 grains in 4 fluid ounces of dried almond-oil constituting Phosphorated Oil (*Oleum Phosphoratum*, B.P.). A mixture, or perhaps a solution, of phosphorus in balsam of tolu and yellow wax with curd soap, forms the official Phosphorus Pill (*Pilula Phosphori*, B.P.).

Granulated or pulverulent phosphorus is obtained by placing a portion under equal parts of spirit and water in a bottle, standing the bottle in warm water till the phosphorus melts, then inserting the stopper (glass, not cork), and shaking the whole till cold.

Red or Amorphous Phosphorus.—Ordinary phosphorus kept at a temperature of about 450° Fahr., in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500°

Fahr. It is used in the manufacture of several varieties of lucifer-matches, not emitting the poisonous jaw-destroying fumes given off by ordinary phosphorus.

Quantivalence.—The atom of phosphorus is quinquivalent, as seen in the pentachloride (PCl_5) and oxychloride ($POCl_3$); but it often exhibits trivalent activity, as seen in the trichloride (PCl_3) and trihydride (PH_3).

Molecular weight.—Phosphorus is an exception to the rule that the atomic weights (in grains, grammes, etc.) of elements occupy similar volumes of vapour at similar temperatures, the equivalent weight of phosphorus (31) only giving half such a volume. Hence, while the molecular weights, that is, double the atomic weights, of oxygen ($O_2=32$), hydrogen ($H_2=2$), nitrogen ($N_2=28$), etc., give a similar bulk of vapour at any given temperature, the double atomic weight of phosphorus ($P_2=62$) only gives half this bulk; that is, four times the atomic weight of phosphorus must be taken to obtain the whole bulk. It would appear, therefore, that the molecule of phosphorus contains four atoms $P_4=124$. As with sulphur, however, phosphorus in the state ordinarily known to us may be abnormal, and conditions yet be found in which the molecular weight is double the atomic weight.

Phosphoric Acid.

The chief use of phosphorus in pharmacy is for the production of Diluted Phosphoric Acid. Phosphorus is boiled with nitric acid and water until dissolved. The solution, evaporated to a low bulk to remove nitrous compounds and diluted until the product has a specific gravity of 1·5, contains about two-thirds of real acid (H_3PO_4) and one-third water, and is the *Acidum Phosphoricum Concentratum*, B.P. The latter, diluted so as to contain nearly 14 (13·8) per cent. of acid (H_3PO_4), equivalent to 10 per cent. of phosphoric anhydride (P_2O_5), constitutes the *Acidum Phosphoricum Dilutum*, B.P., a colourless sour liquid of specific gravity 1·08. If the necessary appliances are at hand, specimens may be prepared by the official process as follows:—Three-quarters of an ounce of the *concentrated*, or a quarter of a pint of the *diluted*, is made by boiling together, in a flask attached to a vertical condenser, 103 grains of phosphorus, 1½ fluid ounces of the official nitric acid, and 2 ounces of water. By some such arrangement the condensed products are returned to the flask. The operation is continued until the phosphorus has disappeared.

$$\underset{\text{Phosphorus.}}{3P_4} + \underset{\text{Nitric acid.}}{20HNO_3} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Phosphoric acid.}}{12H_3PO_4} + \underset{\text{Nitric oxide.}}{20NO}$$

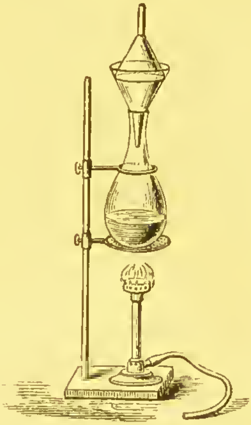
The liquid remaining in the flask is then transferred to a dish (preferably of platinum), evaporated down to about half an ounce, and lastly, diluted with distilled water.

The use of the water in the former part of the process is to moderate the reaction. Strong hot nitric acid oxidizes phosphorus with almost explosive rapidity, hence the acid must be diluted in the first instance, and the dilution be maintained to prevent its becoming too strong by loss of water. Time is saved by using a strong acid, but in that case constant supervision is necessary in order that water may be added, or the temperature otherwise reduced, should the action become too violent. Deficiency of nitric acid must also be avoided, or some phosphorous acid (H_2PHO_3) will be formed.

Markoe, also to economize time, modifies the process by adding for every ounce of phosphorus 4 or 5 grains of iodine, and, drop by drop, 25 or 30 drops of bromine. The iodine and bromine unite with the phosphorus with a readiness or even violence that would be explosive if not controlled by the presence of the cold fluids,—further cooled, if necessary, by immersing the vessel in cold water. Iodide of phosphorus (PI_5) and bromide of phosphorus (PBr_5) are at once formed. These in the presence of water immediately yield hydriodic and hydrobromic acids (HI, HBr) and phosphoric acid. The nitric acid attacks the hydriodic and hydrobromic acids, forming the lower oxides of nitrogen, which escape as gas, water, and free iodine and bromine. The latter unite with more phosphorus, and the reactions are repeated. This carrying power of a little iodine or bromine or both would perhaps be indefinitely prolonged if no vapour of these elements or their acids escaped with the gases. The phosphorus having disappeared, excess of nitric acid is got rid of roughly by dropping in clean rags or paper (nitric oxide, carbonic acid gas, and water being formed) and, the last portions, by adding oxalic acid (which even still more readily yields similar products). Evaporation to a syrupy consistence finally removes all traces of iodine, bromine, oxalic acid, and moisture. The product is then diluted to any required extent.

Experimental process.—A flask, in the neck of which a funnel is inserted, and a second funnel inverted, so that its mouth rests within the mouth of the first, is an efficient and convenient arrangement of apparatus for the official process, especially if the operation be conducted slowly. (*See* fig. 40.)

Fig. 40.



Solution of phosphoric acid evaporated to a sp. gr. of 1·850 yields a mass of prismatic crystals of H_3PO_4, especially if a crystal or two be dropped into the fluid (Cooper). Further evaporated, it leaves a residue which melts at a low red heat, yielding *pyrophosphoric acid*, and finally, *metaphosphoric acid* (*Glacial Phosphoric Acid*).

A commercial variety of phosphoric acid, containing no large amount of impurity, is prepared by well digesting a mixture of bone-ash, sulphuric acid, and water; filtering, concentrating, precipitating calcium by strong sulphuric acid; and heating until sulphuric vapours cease to escape. Also by burning phosphorus to phosphoric anhydride, dissolving the latter in water, and boiling with a little nitric acid to oxidize any lower acids of phosphorus and to cause any meta- or pyro-phosphoric acid to take up the elements of water.

Prepared from bones, phosphoric acid is apt to develop fungoid deposits (Jensen). Prepared from phosphorus, it occasionally contains arsenium in the form of arsenic acid. The latter is detected and removed, together with any traces of platinum or lead, on passing sulphuretted hydrogen through the warmed acid.

Quantivalence.—The elements represented by the formula PO_4 are those characteristic of phosphates. The grouping is trivalent; hence there may exist trimetallic phosphates (M'_3PO_4), dimetallic acid phosphates ($M_2'HPO_4$) or monometallic acid phosphates ($M'H_2PO_4$) and, lastly, trihydric phosphate (H_3PO_4), or common phosphoric acid. These are the ordinary phosphates, or *orthophosphates*, met with in nature or used in pharmacy; the rarer pyrophosphates and metaphosphates, as well as the phosphites and hypophosphites, will be mentioned subsequently. Crude dry phosphate of calcium ground with sulphuric acid yields the very largely used artificial manure termed "superphosphate." It contains acid phosphate of calcium (CaH_42PO_4, $2H_2O$) and sulphate of calcium ($CaSO_4$, $2H_2O$).

Analytical Reactions (Tests).

First Analytical Reaction.—To an aqueous solution of a phosphate (*e.g.* Na_2HPO_4) add solution of sulphate of magnesium with which chloride of ammonium and ammonia have been mixed; a white crystalline precipitate falls (ammonio-magnesian phosphate, $MgNH_4PO_4$).

Chloride of ammonium is added to prevent the precipitation of hydrate of magnesium. Arseniates, which have close analogy to phosphates, give, with the magnesian reagent, a precipitate of similar character.

Second Analytical Reaction.—To an aqueous solution of a phosphate add solution of nitrate of silver; light yellow phosphate of silver (Ag_3PO_4) is precipitated—completely, if the mixture be neither acid nor alkaline. To a portion of the precipitate add ammonia; it dissolves. To another portion add nitric acid; it dissolves. By the former part of this reaction phosphates may be distinguished from their close allies, the arseniates, arseniate of silver being of a chocolate colour.

Third Analytical Reaction.—To a solution (in a few drops of acid) of a phosphate insoluble in water (*e.g.* Ca_32PO_4) add the acetate of an alkali metal (easily made by adding to soda or ammonia in a test-tube excess of acetic acid), and then a drop or two of solution of perchloride of iron; a yellowish white precipitate falls (ferric phosphate, Fe_22PO_4), insoluble in acetic acid. Too much of the ferric chloride must not be added, or ferric acetate will be produced, in which the ferric phosphate is to some extent soluble.

To remove the whole of the phosphoric radical from the solution add ferric chloride so long as a precipitate is produced, and boil; ferric phosphate and oxyacetate are precipitated.

To obtain confirmatory evidence of the presence of phosphate in this precipitate, and to separate the phosphoric radical as a more characteristic phosphate, collect the precipitate on a filter, wash, drop some solution of ammonia on it, then sulphydrate of ammonium, and finally wash with water; black ferrous sulphide remains on the filter, while phosphate of ammonium occurs in the filtrate. To the filtrate add a mixture of solutions of sulphate of magnesium and chloride of ammonium, and well stir; a granular precipitate (ammonio-magnesian phosphate) appears.

Fourth Analytical Reaction.—In diluted nitric acid dissolve a little phosphate of calcium (or any other phosphate) and then add solution of molybdate of ammonium, and gently heat; a yellow precipitate falls.

This precipitate contains what is somewhat indefinitely termed phospho-molybdic acid—a compound of molybdic acid with phosphoric acid (about 4 per cent. of H_3PO_4) with ammonia (nearly 7 per cent.).

Molybdate of ammonium is obtained by roasting the native sulphide of molybdenum (MoS_2) to molybdic oxide or anhydride (MoO_3), dissolving the latter in water, adding ammonia, evaporating and crystallizing.

Molybdates having the following formulæ ($M = 1$ univalent atom of any metal) have been obtained:—M_2MoO_4; $MHMoO_4$; $MHMoO_4,H_2MoO_4$. According to Carington, commercial molybdate of ammonium is commonly the intermediate of the three salts.

Note.—The foregoing two reactions are useful in the analysis of bone-earth, of other earthy phosphates, phosphate of iron, and all phosphates insoluble in water. Only arseniates give similar appearances; but the acid solution of these may be decomposed by agitation with sulphurous acid, ebullition and subsequent treatment with sulphuretted hydrogen —yellow arsenious sulphide, As_2S_3, being then precipitated.

Other Analytical Reactions.—Solutions of barium and calcium salts give, with aqueous solutions of phosphates, white precipitates (of the respective phosphates $BaHPO_4$, or Ba_32PO_4, and $CaHPO_4$, or Ca_32PO_4), all of which are soluble in acetic and the stronger acids.

QUESTIONS AND EXERCISES.

State the source of phosphorus.—Give equations or diagrams explanatory of the isolation of phosphorus from its natural compounds.—What is the composition of farmers' "superphosphate," and how is it prepared? Enumerate the properties of phosphorus.—Mention some solvents of phosphorus.—How are the official varieties of phosphoric acid made? Describe the precautions to be observed in making this acid.—What are the strengths of the official acids?—Write formulæ illustrative of all classes of orthophosphates.—Mention the chief tests for soluble and insoluble phosphates.—By what reactions may phosphates be distinguished from arseniates?

VANADIUM, V, 51·3, is a very rare element, and is here mentioned only because of its exceedingly interesting relationship to nitrogen, phosphorus, arsenium, and antimony; it with them forming five closely connected members of one family. Discovered, but not isolated, by Sefström, and its compounds investigated by Berzelius, it has only of late years been obtained in the free state and fully studied by Roscoe.

N_2O_5, N_2O_4, N_2O_3, N_2O_2, N_2O. V_2O_5, V_2O_4, V_2O_3, V_2O_2, V_2O.

Orthophosphates .	R'_3PO_4	Orthovanadates .	R'_3VO_4
Pyrophosphates .	$R'_4P_2O_7$	Pyrovanadates .	$R'_4V_2O_7$
Metaphosphates .	$R'PO_3$	Metavanadates .	$R'VO_3$

Isomorphous Minerals.

Apatite	$3(Ca_32PO_4)$, CaF_2
Pyromorphite	$3(Pb_32PO_4)$, $PbCl_2$
Mimetesite	$3(Pb_32AsO_4)$, $PbCl_2$
Vanadinite	$3(Pb_32VO_4)$, $PbCl_2$

BORIC ACID AND OTHER BORATES.

Formula of Boric Acid, H_3BO_3. Molecular weight, 62.

The composition of artificial boric acid, sometimes termed *boracic acid*, is expressed by the formula H_3BO_3; but at a temperature of 212° F. this body loses the elements of water and yields metaboric acid, HBO_2, which, at higher temperatures, becomes boric anhydride (B_2O_3). Metaboric acid exists in the jets of steam (*fumerolles*, or *suffioni*) that issue from the earth in some districts of Tuscany, and collects in the water of the *lagoni* (lagoons or little lakes) formed at the orifices of the steam channels. This acid liquid, evaporated by aid of the waste natural steam and neutralized by carbonate of sodium, gives common borax, possibly a metaborate of sodium and of hydrogen, with water of crystallization ($2NaBO_2,2HBO_2,9H_2O$); or possibly a metaborate of sodium with boric anhydride ($2NaBO_2,B_2O_3,10H_2O$); or possibly a pyroborate of sodium ($Na_2B_4O_7,10H_2O$), analogous to the pyrochromate of potassium ($K_2Cr_2O_7$) or pyrosulphuric acid ($H_2S_2O_7$). It is sometimes termed biborate of sodium. It occurs "in transparent colourless crystals, occasionally slightly effloresced, with a weak alkaline reaction; insoluble in rectified spirit, soluble in water." Native borax, or *tincal*, and other borates, are also found in Thibet, Nevada, Peru, Chili, and, recently, in California in the Colorado district. The introduction of the natural borax from California has reduced the price to about one-half its former amount. The Californian borax is represented as forming large portions of the crystalline bed of a dried-up lake. Borax is also largely made by boiling native borate of calcium with carbonate of sodium.

Fused borax readily dissolves metallic oxides, as will have been noticed already in testing for cobalt and manganese. Hence, besides its use in medicine (*Borax*, B.P.; *Mel Boracis*, B.P., and *Glycerinum Boracis*, B.P.), it is employed as a flux in refining and other metallurgic and ceramic operations.

Quantivalence.—The boric radical is trivalent (BO_3'''); the metaboric, univalent (BO_2').

The element boron, like carbon, occurs in the amorphous, graphitoidal, and crystalline conditions. It is a trivalent element (B'''), yielding definite salts, such as the chloride (BCl_3) and fluoride (BF_3). Its atomic weight is 11.

REACTIONS.

First Synthetical Reaction.—To a hot solution of a crystal of borax add a few drops of sulphuric acid and set aside; on cooling, crystalline scales of boric acid (H_3BO_3) (*Acidum Boricum*, B.P.) are obtained. They may be purified by collecting on a filter, slightly washing, drying, digesting in hot alcohol, filtering, and setting aside; pure boric acid is deposited. The acid may also be recrystallized from water. Fifty grains dissolved in one ounce of rectified spirit constitutes "Solution of Boric Acid," B.P.

Boric acid occurs in "colourless, pearly, lamellar crystals; unctuous to the touch; taste feebly sour and bitter and leaving a sweetish after-flavour in the mouth. Soluble in 25 parts of water, 5 of glycerine, 16 of rectified spirit at 60° F. (15·5° C.), and in 3 of boiling water. It changes the colour of litmus to wine-red; turmeric paper, moistened with an aqueous solution slightly acidified with hydrochloric acid, becomes brownish-red on gently drying, and this colour changes to a greenish if solution of potash be added. The alcoholic solution burns with a flame tinged with green. The crystals liquefy when warmed, and on careful ignition lose $43\frac{1}{2}$ per cent. of their weight, the product solidifying, on cooling, to a brittle glass-like mass."

Boric acid is a very weak compound. Indeed the alkalinity of borax is as great as if it contained no acidulous material. The acid only slowly decomposes carbonates.

Second Synthetical Reaction.—Mix together 1 part of boric acid, 4 parts of acid tartrate of potassium, and 10 or 20 of water; evaporate to a syrupy consistence, spread on plates and set aside for dry scales to form. The resulting substance is, in water, far more readily soluble than either of its constituents, and is known as *boro-tartrate of potassium*, or *soluble cream of tartar*. The Prussian *tartarus boraxatus* differs from the foregoing French variety in containing 1 part of *borax* to 3 of acid tartrate of potassium.

ANALYTICAL REACTIONS (TESTS).

First Analytical Reaction.—Dip a piece of turmeric paper

(paper soaked in tincture of turmeric tubers and dried) into a solution of boric acid; it is coloured brown-red, as by alkalies.

The usual way of applying this test is as follows:—Add to a solution of any borate a few drops of hydrochloric acid, immerse half of a slip of turmeric paper in the liquid, then remove the hydrochloric acid by drying the paper over a flame. Concentrated hydrochloric acid and ferric chloride produce a somewhat similar effect.

Second Analytical Reaction.—To a fragment of a borate, or metaborate (borax, for example) in a small dish or watch-glass, add a drop of sulphuric acid and then a little alcohol, warm the mixture and set light to the spirit; the resulting flame will be tinged of a greenish colour at its edges by the volatilized metaboric acid or boric anhydride.

The liquid should be well stirred while burning. Salts of copper and some metallic chlorides produce a somewhat similar colour. The flame-test may also be applied to a little of a mixture of the borate with strong sulphuric acid on a platinum wire. Glycerine may be used in place of sulphuric acid (Iles), the reaction with borax being, according to Dunstan, the formation of borate of glyceryl, $C_3H_5BO_3$, water, and metaborate of sodium, the borate of glyceryl and water reacting immediately to form boric acid and glycerine.

Other Analytical Reactions.—In solutions of borax, barium salts give a white precipitate (barium metaborate, $Ba2BO_2$), soluble in acids and alkaline salts. Nitrate of silver also affords a white precipitate (metaborate of silver, $AgBO_2$), soluble in nitric acid and in ammonia. Chloride of calcium, if the solution is not too dilute, gives a white precipitate (borate of calcium, $CaBO_2$).

QUESTIONS AND EXERCISES.

Illustrate the relation of vanadium to nitrogen by formulæ of compounds of each element.—Describe the preparation of borax.—Give the formulæ of boric acid, metaboric acid, and borax.—Mention the tests for borates or metaborates.

The foregoing acids and other salts contain the only acidulous radicals that are commonly *met with in analysis or in ordinary medical or pharmaceutical operations. There are, however, many others which* occasionally *present themselves. The chief of these will now be shortly noticed; they are arranged in alphabetical order to facilitate reference.*

SALTS OF RARER ACIDULOUS RADICALS.

BENZOIC ACID ($HC_7H_5O_2$) AND OTHER BENZOATES.—Slowly heat a fragment of benzoin (Gum Benjamin) (*Benzoinum*, B.P.) in a test-tube; benzoic acid (*Acidum Benzoicum*, B.P.) rises in vapour and condenses in small, white, feathery plates and needles on the cool sides of the tube. If the benzoin is first mixed with twice its weight of sand or roughly powdered pumice-stone, and the heat very cautiously applied, the product will be less likely to be burnt, and a larger quantity will be yielded. By repeated sublimation 10 to 15 per cent. may be obtained.

A more economical process is to boil the benzoin with one-fourth its weight of lime, filter, concentrate, decompose the solution of benzoate of calcium by hydrochloric acid, collect the precipitated benzoic acid, press between paper, dry, and sublime in a tube or other vessel.

$$\underset{\substack{\text{Benzoic acid}\\\text{(impure).}}}{2HC_7H_5O_2} + \underset{\substack{\text{Hydrate of}\\\text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Benzoate of}\\\text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\substack{\text{Benzoate of}\\\text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Chloride of}\\\text{calcium.}}}{CaCl_2} + \underset{\substack{\text{Benzoic acid}\\\text{(pure).}}}{2HC_7H_5O_2}$$

There is always associated with the product a minute quantity of a mixture of volatile oils of agreeable odour, suggesting that of hay, and yielding, according to Jacobsen, methyl benzoate, guaiacol (methoxycatechol), catechol, acetylguaiacol, benzyl benzoate, benzophenone, and benzoylguaiacol.

Benzoic acid is also prepared on a large scale artificially from naphthalin, one of the crystalline by-products in the distillation of coal for gas. The naphthalin is oxidized by nitric acid to naphthalic or phthalic acid :—

$$\underset{\text{Naphthalin.}}{C_{10}H_8} + \underset{\text{Oxygen.}}{4O_2} = \underset{\text{Phthalic acid.}}{H_2C_8H_4O_4} + \underset{\text{Oxalic acid.}}{H_2C_2O_4}$$

The phthalic acid is neutralized by lime and the phthalate of calcium heated with hydrate of calcium in a covered vessel at a temperature of about 640° F. for several hours. Benzoate and carbonate of calcium are formed, and, from the powder, the benzoic acid is set free by action of hydrochloric acid.

$$\underset{\substack{\text{Phthalate of}\\ \text{calcium.}}}{2CaC_8H_4O_4} + \underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{Ca2HO} = \underset{\substack{\text{Benzoate of}\\ \text{calcium.}}}{Ca2C_7H_5O_2} + \underset{\substack{\text{Carbonate of}\\ \text{calcium.}}}{2CaCO_3}$$

The crystalline deposit formed when essential oil of almonds (benzoic aldehyde) is exposed to the air is benzoic acid.

$$\underset{\text{Benzoic aldehyde.}}{2C_6H_5COH} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Benzoic acid.}}{2C_6H_5COOH \text{ or } 2HC_7H_5O_2}$$

Pure sublimed benzoic acid is also obtained from hippuric acid (p. 402). Such acid, if not thoroughly purified, may have an urinoid odour.

Jacobsen has prepared benzoic acid from benzotrichloride (trichloromethylbenzene, $C_6H_5CCl_3$), one of the trichlorotoluenes, by heating with glacial acetic acid and chloride of zinc. This acid, if not very highly purified, may give a green colour to flame when placed on platinum wire with a little oxide of copper. In artificial benzoic acid the fragrant volatile oil characteristic of the acid from benzoin is, of course, absent.

Official benzoates.—To a little benzoic acid add a few drops of solution of ammonia or of carbonate of sodium; it readily dissolves, forming corresponding benzoates (*Ammonii Benzoas*, B.P., *Sodii Benzoas*, B.P., $NaC_7H_5O_2$).

$$\underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Ammonia.}}{NH_4HO} = \underset{\text{Benzoate of ammonium.}}{NH_4C_7H_5O_2} + \underset{\text{Water.}}{H_2O}$$

On evaporation, acid crystals or, ammonia being added, neutral crystals of benzoate of ammonium are deposited.

Properties.—Benzoic acid is also soluble in other alkaline liquids, forming benzoates. It is slightly soluble in cold water, more so in hot, and readily soluble in rectified spirit. It melts at 248° F. and boils at 462°, volatilizing with only a slight residue. Heated with lime it yields benzene. It dissolves in cold sulphuric acid without decomposition; is again deposited on dilution; and the traces of odoriferous and other substances present in the acid from benzoin only slightly colour the fluid, even on gently warming.

Tests for benzoates.—To a portion of a solution of a benzoate add a drop or two of sulphuric or hydrochloric acid; a white crystalline precipitate (benzoic acid) separates. To another portion, carefully made neutral, add a drop or two of neutral solution of perchloride of iron; a reddish precipitate (ferric benzoate) results.

Cinnamic acid (C_8H_7COOH).—Benzoic acid is distinguished from an allied body, cinnamic acid (occurring in Balsams of Peru, Tolu, and Storax, and sometimes in Benzoin), by not yielding benzaldehyde (C_6H_5COH) (oil of bitter almonds) when distilled with chromic acid—that is, with a mixture of red chromate of potassium and sulphuric acid, or when rubbed with half its weight of permanganate of potassium. ——Old hard balsam of tolu yields cinnamic acid on boiling with lime and water and precipitating by hydrochloric acid. ——Jacobsen makes it artificially by the prolonged reaction of glacial acetic acid and benzodichloride in the presence of chloride of zinc.

Carminic Acid ($C_{14}H_{14}O_8$).—This is the colouring principle (about 10 per cent.) of the dried female *Coccus Cacti*, or cochineal (*Coccus*, B.P.). The *carmine* of trade, when unadulterated (*vide Pharmaceutical Journal*, 1859–60, p. 546), is carminic acid united with two or three per cent. of alumina and lime, or, occasionally, of oxide of tin or albumen. It should be wholly soluble in solution of ammonia, giving an apparently clear, rich purple liquid. Carmine with French chalk, or starch, constitutes *face rouge* or *animal rouge*.

Merrick tests the relative value of several samples of cochineal or carmine by observing how much solution of permanganate of potassium is required to change the colour of a decoction to faint pink. The silvery coating of cochineal is a wax, *coccerin*.

CETRARIC ACID ($H_2C_{34}H_{30}O_{16}$) is the bitter principle of Iceland "moss" (*Cetraria*, B.P.). In the lichen it is associated with much starch.

CHRYSOPHANIC ACID ($C_{15}H_{10}O_4$).—This yellow acid is found in various species of rhubarb-root (*Rhei Radix*, B.P.) and, under the name of *parietinic acid*, in various common yellow lichens. Kubli considers, Dragendorff also, that the chrysophanic acid of rhubarb is only produced when a glucoside, *chrysophan*, is acted on by a ferment in the presence of water. The formation of chrysophanic acid is probably, in most if not in all cases, preceded by the occurrence of *chrysophan* or an allied body. The author found it in "Chrysarobin," a name given by Kemp to the pith, etc., of a leguminous tree (*Andira araroba*), and now official (*Chrysarobinum*, B.P.). Chrysarobin is also known as Araroba Powder, Bahia Powder, Brazil Powder, Goa Powder, and Ringworm Powder. The chrysarobin, as it occurs in the tree, or when fresh, has been shown by Liebermann and Seidler to have the formula $C_{30}H_{26}O_7$; this, by oxidation and elimination of water, yields the chrysophanic acid, more or less of which occurs with the chrysarobin, according to the age of the chrysarobin and to, perhaps, the presence or absence of a ferment. A solution of chrysarobin in alkali rapidly absorbs oxygen, the fluid yielding chrysophanic acid. Chrysophanic acid may be obtained in crystals of a golden-yellow colour, hence the name (from χρυσὸς, *chrusos*, gold, and φαίνω, *phainō*, I shine). Its synonyms are *Rhaponticin*, *Rheic acid*, *Rhein*, *Rheumin*, *Rhubarbaric acid*, *Rhubarbarin*, *Rumicin*. Chrysophanic acid, actual or potential, black, red-brown, and red resins (*Aporetine*, *Phæoretine*, and *Erythroretine*), a bitter principle, and tannic acid are considered to be the conjoint source of the therapeutic properties of rhubarb. Chrysophanic acid may also be obtained from several species of *Rumex* or *Dock*. "Rumicin" is a preparation of Yellow Dock. *Cascara Sagrada*, or Sacred Bark (*Rhamni Purshiani Cortex*, B.P.), according to Limousin, contains chrysophanic acid; a glucoside (?), a ferment, and various resins being also said to be present.

Emodin, $C_{15}H_{10}O_5$, is apparently closely associated, chemically, with chrysophanic acid. It is obtained with chrysophanic acid in the preparation of the latter from rhubarb. It also occurs in Black Alder bark (*Rhamni Frangulæ Cortex*, B.P.), according to Liebermann and Waldstein. It is said to be derived, together with glucose, from *frangulin*, $C_{21}H_{20}O_9$, the glucoside of the dried bark.

CYANIC ACID (HCNO) AND OTHER CYANATES.—The reducing-power of cyanide of potassium (KCN) (or ferrocyanide, $K_4FeC_6N_6$) on metallic compounds, is due to the avidity with which it absorbs oxygen and forms cyanate (KCNO).

Process.—Fuse a few grains of cyanide of potassium in a small porcelain crucible, and add powdered oxide of lead; a globule of metallic lead is at once set free, excess of the oxide converting the whole of the cyanide of potassium into cyanate of potassium.

Urea.—Cyanate of potassium (KCNO), or, better, cyanate of lead (Pb2CNO), treated with sulphate of ammonium, yields cyanate of ammonium (NH_4CNO); and solution of cyanate of ammonium, when simply heated, changes to artificial *urea* (CH_4N_2O), the most important constituent of urine, and the chief form in which the nitrogen of food is eliminated from the animal system. The process will be more fully described subsequently in connection with urea.

FORMIC ACID ($HCHO_2$).—The red ant (*Formica rufa*) and several other insects, when irritated, eject a strongly acid, acrid liquid, having a composition expressed by the above formula, and which has appropriately received the name of formic acid; it is also contained in the leaves of the stinging-nettle. (According to Church, the sting of the *wasp* is *alkaline*.)

Process.—It may be artificially prepared by heating equal weights of oxalic acid and glycerine to a temperature of from 212° F. to 220° for fifteen hours, and then distilling the mixture with a considerable volume of water. The formic acid slowly passes over, glycerine being regenerated. The dilute acid may be concentrated by neutralizing with carbonate of lead, filtering, evaporating to a small bulk, collecting the deposited crystalline formate of lead, drying, decomposing in a current of dry sulphuretted hydrogen, at 212° F., and rectifying the resulting syrupy acid from dry formate of lead. It should be fluid at 48° F. and boil at 212° F. The following are the chief reactions:—

$$\underset{\text{Glycerine.}}{C_3H_53HO} + \underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Hydrato-oxalate of glyceryl.}}{C_3H_5HOC_2O_4} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\substack{\text{Hydrato-oxalate}\\\text{of glyceryl.}}}{C_3H_5HOC_2O_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Glycerine.}}{C_3H_53HO} + \underset{\substack{\text{Formic}\\\text{acid.}}}{HCHO_2} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2}$$

Formic Acid may be instructively though not economically prepared by the oxidation of methylic alcohol (wood-spirit), just as acetic acid and valerianic acid are obtained from ethylic alcohol and amylic alcohol respectively.

$$\underset{\text{Methylic alcohol.}}{CH_3HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Formic acid.}}{HCHO_2} + \underset{\text{Water.}}{H_2O}$$

Tests.—Formic acid does not char when heated alone or with sulphuric acid, but splits up into carbonic oxide gas and water. It is recognised by this property and by its reducing-action on salts of gold, platinum, mercury and silver. It is solid below 32° F.

GALLIC ACID.—*See* TANNIC ACID.

HEMIDESMIC ACID.—The supposed active principle of hemidesmus root (*Hemidesmi Radix*, B.P.).

HIPPURIC ACID ($HC_9H_8NO_3$) is a constituent of human urine (much increased on taking benzoic acid), but is prepared from the urine of the horse (hence the name, from ἵππος, *hippos*, a horse), or, better, from that of the cow. To such urine add a little milk of lime, boil for a few minutes, remove precipitated phosphates by filtration, drop in hydrochloric acid until the liquid, after well stirring, is exactly neutral to test-paper, concentrate to about one-eighth the original bulk, and add excess of strong hydrochloric acid; impure hippuric acid is deposited. From a solution of the impure acid in hot water chlorine gas removes the colour, and the liquid deposits crystals of pure hippuric acid on cooling.

Tests.—To a solution of a hippurate add neutral solution of ferric chloride; a brown precipitate (ferric hippurate) results. Salts of silver and mercury give white precipitates. Heat hippuric acid in a test-tube; it chars, benzoic acid sublimes, and vapours of characteristic odour are evolved; they contain, amongst other bodies, hydrocyanic acid and a substance smelling somewhat like Tonka bean.——The crystalline form of hippuric acid is characteristic; it will be described in connection with the subject of urine.

QUESTIONS AND EXERCISES.

Give the preparation, composition, properties, and tests of benzoic acid, employing equations or diagrams.—What is the nature of carmine?—Name the bitter principle of Iceland "moss."—Mention the colouring principle of rhubarb.—To what is rhubarb considered to owe its medicinal activity?—How is cyanate of potassium prepared, how converted into an ammonium salt, and what are the relations of the latter to urea?—Give the formulæ of cyanic acid, cyanate of ammonium, and urea.—What is the chemical formula of formic acid?—Describe the artificial production of formic acid.—Describe the relation of formic acid to wood-spirit.—State the sources, characters, and tests of hippuric acid.

HYDROFERROCYANIC ACID ($H_4Fe''Cy_6$, or H_4Fcy'''') AND OTHER FERROCYANIDES.—The ferrocyanide of most interest is that of potassium, the "yellow prussiate of potash" (*Potassii Ferrocyanidum*, B.P.) ($K_4FeC_6N_6$, $3H_2O$), the formation of which was alluded to in connection with hydrocyanic acid (*see* p. 324). It cannot be regarded as simply a double salt of cyanide of potassium with cyanide of iron ($FeCy_2$, $4KCy$), its chemical properties being entirely different from either of those substances; moreover, unlike cyanide of potassium, it is not poisonous. Most of the reactions point to the conclusion that its iron and cyanogen are intimately united to form a definite quadrivalent radical appropriately termed *ferrocyanogen* (FeC_6N_6, or Fcy). One part of ferrocyanide of potassium in 20 of water forms the official "Solution of Ferrocyanide of Potassium," B.P.

Tests.—Many of the ferrocyanides are insoluble, and are therefore precipitated when solution of ferrocyanide of potassium is added to the various salts. Those of iron and copper being of characteristic colour, are adopted as tests of the presence of the metals or of the ferrocyanogen, as the case may be. To solution of ferrocyanide of potassium add a ferric salt; a dark blue precipitate (ferrocyanide of iron, Fe_4Fcy_3; Prussian blue) falls. To another portion add solution of a copper salt; a reddish-brown precipitate (ferrocyanide of copper, Cu_2Fcy) results.

Note.—The ferrocyanogen in ferrocyanide of potassium is broken up when the salt is heated with sulphuric acid, *carbonic oxide* being evolved if the acid is strong (that is, ordinary oil of vitriol—H_2SO_4 with 2 or 3 per cent. of water), and *hydrocyanic acid* if weak:—

$$K_4FeC_6N_6, 3H_2O + 3H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

$$2K_4FeCy_6 + 6H_2SO_4 + xH_2O = FeK_2FeCy_6 + 6KHSO_4 + 6HCy + xH_2O.$$

Hydrocyanic Acid has already been described. (*Vide* p. 324.)

Carbonic Oxide (CO).—Heat two or three fragments of ferrocyanide of potassium with eight or ten times their weight of sulphuric acid, and as soon as the gas begins to be evolved, remove the test-tube from the flame; for the action, when once set up, proceeds somewhat tumultuously. Ignite the carbonic oxide at the mouth of the tube; it burns with a pale-blue flame, the product of combustion being carbonic acid gas (CO_2).

Carbonic oxide is a direct poison. It is generated whenever coke, charcoal, or coal burns with an insufficient supply of air. Hence the danger of open fires in the more or less closed apartments of ordinary dwellings.

Carbonic oxide may also be obtained from oxalic acid. (*Vide* p. 373.)

HYDROFERRICYANIC ACID ($H_6Fe'''_2Cy_{12}$, or H_6Fdcy^{vi}) and OTHER FERRICYANIDES.—Pass chlorine gas slowly through solution of ferrocyanide of potassium until the liquid, after frequent shaking, ceases to give a blue precipitate when a minute portion is taken out on the end of a glass rod and brought into contact with a drop of dilute solution of a ferric salt; it now contains ferricyanide of potassium (B.P.) ($K_6Fe'''_2Cy_{12}$, or K_6Fdcy^{vi}), *red prussiate of potash*, as it is termed, from the colour of its crystals. Excess of chlorine must be carefully avoided, as chloride of cyanogen and other compounds are then formed. (Such a result does not ensue if bromine be used instead of chlorine, but the process is less economical. Other processes are known.)

$$2K'_4Fe''Cy'_6 + Cl'_2 = 2K'Cl' + K'_6Fe_2'''Cy'_{12}.$$

Note.—The removal of two atoms of potassium from the ferrocyanide molecules is the only change of composition that occurs; but the ferrocyanogen is altered in quality, its iron passing from the ferrous to the ferric condition, from bivalent to trivalent activity—altered to a condition in which it no longer precipitates ferric salts, but gives a dark-blue precipitate with ferrous salts.

The radical is distinguished as *ferricyanogen.*

Test.—To some of the solution add solution of ferrous sulphate; a dark-blue precipitate falls. This precipitate is ferricyanide of iron (Turnbull's blue), $Fe''_3Fe'''_2Cy'_{12}$, or $Fe''_3 Fdcy^{vi}$.

$$K_6Fdcy + 3FeSO_4 = Fe_3Fdcy + 3K_2SO_4.$$

It will be noticed that the change in the condition of the iron keeps up the balance of the atomic values of the various parts of the radicals or of the salts; the quantivalential equilibrium is maintained.

A solution of 1 part of ferricyanide of potassium in 20 parts of water constitutes the "Solution of Ferricyanide of Potassium," B.P.

HYDROFLUORIC ACID (HF) AND OTHER FLUORIDES.—Molecular weight of HF, 20. The chief use of hydrofluoric acid is in etching on glass. The operation, performed on the small scale, also constitutes the best test for fluorine, the elementary radical of all fluorides.

Process and Test.—Warm any odd piece of window-glass, having an inch or two of surface, until a piece of beeswax rubbed on one side yields a thin oily film. When cool, make a cross, letter, or other mark on the glass by pressing a pointed piece of wood, a penknife, or file through the wax. Place a few grains of powdered fluor-spar, the commonest natural fluoride, in a porcelain crucible (or a lead cup), add a drop or two of sulphuric acid, cover the crucible with the prepared glass, waxed side downwards, and gently warm the bottom of the crucible in a fume-chamber or in the open air in such a way as not to melt the wax. After a few minutes remove the glass, wash the waxed side by pouring water over it, scrape off most of the wax, then warm the glass and wipe off the remainder; the marks made through the wax will be found to be permanently etched on the glass; the acid has eaten into or *etched* (from the German *ätzen*, to corrode) the glass.

The fluoride of calcium and sulphuric acid yield hydrofluoric acid, thus:—$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. The hydrofluoric acid gas and the silica of the glass then yield gaseous fluoride of silicon (SiF_4), which escapes, and water, thus:—$4HF + SiO_2 = 2H_2O + SiF_4$. The silica being removed from the glass, leaves furrows or etched portions.

Note.—In the experiment just described, the liberated hydrofluoric acid also attacks the siliceous glazing of the porcelain crucible; so that in important cases, where search is made for very small quantities of fluorine, vessels of platinum or lead must be employed.

Uses.—The aqueous solution of hydrofluoric acid, used by etchers, and commonly termed simply hydrofluoric acid, or "fluoric" acid, is prepared in leaden stills and receivers, and kept in leaden or gutta-percha bottles. Except these materials, as well as platinum and fluor-spar, hydrofluoric acid rapidly attacks any substance of which bottles and basins are usually made. It quickly cauterizes the skin, producing a painful, slow-healing sore. A mixture of hydrofluoric acid and fluoride of ammonium, known as "white acid," is also used for etching glass.

Quantivalence.—The atom of fluorine, like that of chlorine, bromine, or iodine, is univalent (F'). The great analogy existing between these radicals extends to their compounds.

Fluorine has been isolated by electrolysing hydrofluoric acid (Moissan). It is a gas having a light greenish-yellow colour, and a penetrating and irritating odour somewhat recalling that of strong hypochlorous acid. It combines with great avidity with all elements except oxygen.

HYPOPHOSPHOROUS ACID (H_3PO_2, or HPH_2O_2) AND OTHER HYPOPHOSPHITES.—Boil together, in a fume-chamber, two or three grains of phosphorus, three or four grains of slaked lime, and about a quarter of an ounce of water, until phosphoretted hydrogen, a spontaneously inflammable, badly smelling gas, ceases to be evolved. The lime must not be in great excess, or the hypophosphite will be converted into phosphate as fast as formed. The mixture, filtered, and excess of lime removed by carbonic acid gas, yields solution of hypophosphite of calcium ($Ca2PH_2O_2$) (*Calcii Hypophosphis*, B.P.). The salt may be obtained in crystals by evaporation and slow cooling.

$$2P_4 + 6H_2O + 3CaH_2O_2 = 3(Ca2PH_2O_2) + 2PH_3.$$

Phosphoretted Hydrogen (PH_3).—The above reaction is also that by which phosphoretted hydrogen, the third hydride of phosphorus, may be prepared. If the gas is to be collected, the phosphorus and water may first be boiled in a flask until a jet of spontaneously inflammable phosphorus vapour escapes, with steam, from the end of the attached delivery-tube. Strong hot solution of caustic potash or soda is next very gradually poured into the flask through a funnel tube previously fitted into the cork, the liquid being kept boiling. Phosphoretted hydrogen is then evolved, and if the delivery-tube dip under water may be collected, or allowed to slowly pass up through the water, bubble by bubble, so as to form the peculiar vortex rings of smoke (phosphoric anhydride) characteristic of the experiment. The spontaneous inflammability is due to the presence of a lower hydride, P_2H_4.

Other hypophosphites ($Mg2PH_2O_2, 6H_2O$; $Fe2PH_2O_2, 6H_2O$; etc.) may thus be obtained from other hydrates, or by double decompositions of the calcium salt and carbonates.

Hypophosphite of Sodium ($NaPH_2O_2, H_2O$) (*Sodii Hypophosphis*, B.P.), the old Hypophosphite of Soda, is made by decomposing solution of hypophosphite of calcium by carbonate of sodium, filtering, and evaporating to dryness. It is a white, granular, deliquescent substance. $Ca2PH_2O_2 + Na_2CO_3 = 2NaPH_2O_2 + CaCO_3$. When heated, the water is first evolved, then hydrogen and spontaneously inflammable phosphoretted hydrogen, and a mixture of pyrophosphate and metaphosphate of sodium remains (Rammelsberg). $5NaPH_2O_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2$.

Hypophosphorous Acid, the hydrogen hypophosphite, may be prepared by decomposing the calcium salt by oxalic acid, or, better, the pure barium salt by sulphuric acid; hypophosphite of quinine by dissolving the alkaloid in hypophosphorous acid, or by decomposing sulphate of quinine by hypophosphite of barium. The latter is obtained on boiling excess of pure hydrate of barium with hypophosphite of ammonium, until all ammonia is evolved. The ammonium salt is formed on bringing calcium hypophosphite and oxalate of ammonium together in presence of a little ammonia.

The hypophosphites are often used in medicine in the form of syrups. The term hypophosphite is in allusion to the smaller amount (ὑπὸ, *hupo*, under or deficiency) of oxygen in these compounds (R'_3PO_2) than in the phosphites (R'_3PO_3), a class of salts having again less oxygen in their molecules than exists in those of the phosphates (R'_3PO_4). The prefix *hypo* has similar significance in such words as hyposulphite and hypochlorite.

Tests.—To a portion of the above solution of hypophosphite of calcium add solution of chloride of barium, chloride of calcium, or acetate of lead; in neither case is a precipitate obtained, whereas soluble phosphates and phosphites yield white precipitates (of phosphate or phosphite of barium, calcium, or lead). To other portions add solutions of nitrate of silver and mercuric chloride; the respective metals are precipitated as by phosphites. To another small portion add zinc and dilute sulphuric acid; hydrogen and phosphoretted hydrogen are evolved as from phosphites. To another portion add sufficient oxalic acid to remove the calcium; filter; to the solution of hypophosphorous acid add solution of sulphate of copper and slowly warm the mixture; a solid brown precipitate results (cuprous hydride, Cu_2H_2): increase the heat to the boiling-point; a gas (hydrogen) is evolved and metallic copper is set free. Add the ordinary nitric solution of a molybdate, or tungstate, to a hypophosphite solution, and then a very little sulphurous acid; a blue precipitate results, or, in very dilute solutions, a blue colour deepened on shaking or gently warming. Heat a small quantity of a solid hypophosphite on the end of a spatula in a flame, and note the resulting phosphorescent light and smell; for it splits up into pyrophosphate, a little metaphosphate, hydrogen, phosphoretted hydrogen, and water, the official hypophosphite of calcium yielding about 80 per cent. of residue.

$$7(Ca2PH_2O_2) = 3Ca_2P_2O_7 + Ca2PO_3 + 6PH_3 + H_2O + 4H_2.$$

Five grains of hypophosphite of calcium, if of good quality, will almost decolourize a solution of twelve grains of permanganate of potassium on boiling the mixture for about ten minutes. Five grains of hypophosphite of sodium should almost decolourize eleven and a half grains of permanganate under similar conditions.

The same effect follows the addition of the permanganate to an acid solution of a phosphite, but not to that of an ortho-, meta-, or pyro-phosphate.

HYPOSULPHUROUS ACID ($H_2S_2O_3$) AND OTHER HYPOSULPHITES.—The only hyposulphite of much interest in pharmacy is the sodium salt (Hyposulphite of Sodium, B.P., the old Hyposulphite of Soda) ($Na_2S_2O_3$, $5H_2O$). Hyposulphites are now more usually termed *Thiosulphates* (*e.g.* H_2SO_3S; Na_2SO_3S); being regarded as *sulphates* (*e.g.* Na_2SO_4) in whose molecules one atom of oxygen is displaced by one of sulphur (*θεῖον*, *theion*, sulphur).

Process.—Heat together gently, or set aside in a warm place, a mixture of solution of sulphite of sodium (Na_2SO_3) and a little powdered sulphur; combination slowly takes place, and hyposulphite of sodium is formed. The solution, filtered from excess of sulphur, readily yields crystals. (The solution of sulphite of sodium may be made by saturating solution of soda with sulphurous acid gas.)

Use of hyposulphite of sodium in quantitative analysis.—In the British Pharmacopœia hyposulphite of sodium is given as a reagent for the quantitative estimation of free iodine in volumetric analysis. To a few drops of iodine-water add cold mucilage of starch; a deep-blue colour (starch iodide) is produced. To the product add solution of hyposulphite of sodium until the blue colour just disappears. This absorption of iodine is sufficiently definite and delicate to admit of application for quantitative purposes. It depends on the combination of the iodine with half of the sodium in two molecules of the hyposulphite, the hyposulphurous radicals of the two molecules apparently coalescing to form a new radical, the tetrathionic (from τέτρας, *tetras*, four, and θεῖον, *theion*, sulphur), tetrathionate of sodium ($Na_2S_4O_6$) and iodide of sodium being formed.

Sulphur Oxyacids.—It will be as well here to give the formulæ of other oxyacids of sulphur, forming with the four already mentioned a series that is as useful as the series of compounds of nitrogen and oxygen in illustrating the soundness of Dalton's atomic theory. The first-named (see table below) (H_2SO_2) is more usually termed hyposulphurous acid, and the fourth ($H_2S_2O_3$) thiosulphuric acid. Moreover, there appears to be an acid ($H_2S_2O_4$), between those having the formulæ $H_2S_2O_3$ and $H_2S_2O_6$, which Bernthsen says is really Schützenberger's hydrosulphurous acid, but which the latter chemist says is probably a distinct acid.

Hydrosulphurous Acid	H_2SO_2	?	$H_2S_2O_4$
Sulphurous Acid	H_2SO_3	Dithionic Acid	$H_2S_2O_6$
Sulphuric Acid	H_2SO_4	Trithionic Acid	$H_2S_3O_6$
Hyposulphurous, or Thiosulphuric Acid	$H_2S_2O_3$	Tetrathionic Acid	$H_2S_4O_6$
		Pentathionic Acid	$H_2S_5O_6$

Use of "Hypo" in Photography.—The sodium hyposulphite is largely used in photography to dissolve chloride, bromide, or iodide of silver off plates which have been exposed in the camera. Prepare a little chloride of silver by adding a chloride (chloride of sodium) to a few drops of solution of nitrate of silver. Collect the precipitated chloride on a filter, wash, and add a few drops of solution of hyposulphite of sodium; the silver salt is dissolved, solution of double hyposulphite of sodium and silver being formed. The solution of this double hyposulphite has a remarkably sweet taste, sweeter than syrup if the solution is strong. The double hyposulphite of sodium and gold has been employed for giving a pleasant tint to photographic prints.

Test.—To solution of a hyposulphite add a few drops of dilute sulphuric or other acid and smell the mixture, cautiously; hyposulphurous acid is set free, but at once begins to decompose into sulphurous acid, recognised by its odour, and free sulphur ($2H_2S_2O_3 = 2H_2SO_3 + S_2$). This reaction constitutes the best test for hyposulphites. Another test of a soluble simple hyposulphite is its power of dissolving chloride of silver with production of a more or less sweet solution.

QUESTIONS AND EXERCISES.

Give the formula of ferrocyanide of potassium.—What is the supposed constitution of ferrocyanide of potassium?—Enumerate the tests for ferrocyanogen.—What are the respective reactions of ferrocyanide of potassium with strong and weak sulphuric acid?—Mention and explain a common source of carbonic oxide in households. What is the product of its combustion?—Write equations or diagrams illustrative of the changes effected in ferrocyanide of potassium during its conversion into ferricyanide.—By what reactions may the presence of a ferricyanide in a solution be demonstrated?—State the difference between Prussian blue and Turnbull's blue.—Describe the source, mode of preparation, chief use of, and test for hydrofluoric acid.—Illustrate by a diagram the preparation of hyposulphite of sodium.—Mention the characteristic reactions of hyposulphite of sodium.—Give the names and formulæ of eight acids, each containing hydrogen, sulphur, and oxygen.

LACTIC ACID ($HC_3H_5O_3$) AND OTHER LACTATES.—Lactic acid occurs naturally in willow bark (Dott). When milk turns sour, its sugar has become converted into an acid appropriately termed lactic (*lac, lactis*). Other saccharine and amylaceous substances also by fermentation yield lactic acid. Neither the hydrogen lactate (lactic acid) nor other lactates are much used in England.

Process.—Lactate of calcium and lactic acid may be prepared as follows:—Mix together eight parts of sugar, one of common cheese, three of chalk, and fifty of water, and set aside in a warm place (about 80° F.) for two or three weeks; a mass of small crystals of lactate of calcium results. Remove these, recrystallize from hot water, decompose by sulphuric acid, avoiding excess, digest in alcohol, filter off the sulphate of calcium, evaporate the clear solution to a syrup; this residue is ordinary lactic acid, *Acidum Lacticum*, B.P., sp. gr. 1·212. Three fluid parts of this acid diluted with water to twenty fluid parts, forms the *Acidum Lacticum Dilutum*, B.P., sp. gr. 1·040.

Test.—No single reaction of lactic acid is sufficiently distinctive to form a test. The crystalline form of the lactate of calcium, as seen by the microscope, is characteristic. The production of this salt, and the isolation of the syrupy acid itself, are the only means, short of quantitative analysis, on which reliance can be placed. Lactic acid is soluble in water, alcohol, and ether, but almost insoluble in chloroform. It is only slightly coloured by cold sulphuric acid. Warmed with permanganate of potassium, it gives the odour of aldehyde.

A variety of lactic acid has been obtained from the juice of flesh; it is termed *sarcolactic* acid (from σὰρξ, σαρκὸς, *sarx*, *sarcos*, flesh). Unlike lactic acid, it is precipitated by solution of sulphate of copper.

Malic Acid ($C_4H_6O_5$) and other Malates (from *malum*, an apple).—The juice of unripe apples, gooseberries, currants, rhubarb-stalks, strawberries, grapes, etc., contains malic acid and malate of potassium. When isolated, it occurs in deliquescent prismatic crystals.

Tests.—Malate of calcium ($CaC_4H_4O_5$) is soluble in water; hence the aqueous solution of malic acid or other malate is not precipitated by lime-water or chloride of calcium; but, on adding spirit of wine, a white precipitate falls, owing to the insolubility of the calcium malate in alcohol. Malates are precipitated by lead-salts; on warming the precipitate (malate of lead) with acetic acid, it dissolves, separating out in acicular crystals on cooling. If the mixture be heated without acid, the precipitate agglutinates and fuses. Hot strong sulphuric acid chars malic acid far less readily than it does nearly all other organic acids.

Asparagin ($C_4H_8N_2O_3$, H_2O).—This proximate principle of plants occurs in many vegetable juices, and doubtless plays a very important part in their nutrition. It is deposited in crystals when the fresh juices of asparagus, marsh-mallow, etc., are rapidly evaporated. It is noticed here because malic acid is readily obtained from it by oxidation, nitrogen being eliminated, and because its exact natural position among chemical substances is not yet well made out. The atoms of its molecule are those of aspartate of ammonium ($NH_4C_4H_6NO_4$), into which it is converted when its solution is long boiled. Decomposed by aid of ferments, asparagin, absorbing hydrogen, yields succinate of ammonium $(NH_4)_2 C_4H_4O_4$.

Meconic Acid ($H_2C_7H_2O_7$, $3H_2O$).—Opium contains meconic acid (from μήκων, *mēkōn*, a poppy) partially combined with morphine. To concentrated infusion of opium, nearly neutralized with ammonia, add solution of chloride of calcium; meconate of calcium is precipitated. Wash the precipitate, place it in a small quantity of hot water; add a little hydrochloric acid; the clear liquid (filtered, if necessary) deposits scales of meconic acid on cooling, *Acidum Meconicum*, B.P.

Tests.—To solution of meconic acid or other meconate, or to infusion of opium, add a *neutral* solution of ferric chloride; a red solution (of meconate of iron) is produced. To a portion of the mixture add solution of corrosive sublimate; the colour is not destroyed: to another portion add hydrochloric acid; the colour is discharged. (These reagents act on sulphocyanate of iron, which is of similar tint, in exactly the opposite manner.) To another portion add a drop of a diluted acid, and boil; the colour is not discharged. (A solution of ferric acetate, which is of similar colour, *is* decomposed in boiling, giving a colourless fluid and a red precipitate—ferric oxy-acetate.)

The normal meconates of potassium, sodium, and ammonium are soluble in water, the acid meconates very slightly soluble; the meconates of barium, calcium, lead, copper, and silver are insoluble in water, but soluble in acetic acid.

METAPHOSPHORIC ACID (HPO_3) AND OTHER METAPHOSPHATES.—Prepare phosphoric anhydride (P_2O_5) by burning a small piece of phosphorus in a porcelain crucible placed on a plate and covered by an inverted test-glass, tumbler, half-pint measure-glass, or some such vessel. After waiting a few minutes for the phosphoric anhydride to fall, pour a little water on the plate and filter the liquid; the product is solution of metaphosphoric acid (from μετὰ, *meta*, a preposition denoting change), $P_2O_5 + H_2O = 2HPO_3$.

Tests.—To solution of metaphosphoric acid add ammonio-nitrate of silver, or to a neutral metaphosphate add solution of nitrate of silver; a white precipitate ($AgPO_3$) is obtained. This reaction sufficiently distinguishes metaphosphates from the ordinary phosphates or orthophosphates (from ὀρθός, *orthos*, straight), as the common phosphates may, for distinction, be termed (which give, it will be remembered, a *yellow* precipitate with nitrate of silver). Another variety of phosphates shortly to be considered, the pyrophosphates, also give a white precipitate with nitrate of silver. To the solution of metaphosphoric acid obtained as above, or by the action of acetic acid on a metaphosphate, add an aqueous solution of white of egg; coagulation of the albumen ensues. Neither orthophosphoric nor pyrophosphoric acid coagulates albumen. Boil the aqueous solution of metaphosphoric acid for some time; on testing the solution, the acid will be found to have been converted into orthophosphoric acid:—

$$HPO_3 + H_2O = H_3PO_4 \text{ (orthophosphoric acid).}$$

The ordinary medicinal phosphoric acid is made from phosphorus and nitric acid, the liquid being evaporated to a syrupy consistence to remove the last traces of nitric acid. It may contain pyrophosphoric and metaphosphoric acids, if the heat employed be high enough to remove the elements of water:—

$$2H_3PO_4 - H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid).}$$
$$H_3PO_4 - H_2O = HPO_3 \text{ (metaphosphoric acid).}$$

On redilution the metaphosphoric acid only slowly reabsorbs water. If, therefore, on testing, metaphosphoric acid be found to be present, the solution should be boiled until conversion to orthophosphoric acid has occurred.

NITROUS ACID (HNO_2) AND OTHER NITRITES.—Strongly heat a fragment of nitrate of potassium or of sodium on a piece of platinum foil; oxygen is evolved and nitrite of potassium or sodium remains.

Test.—Dissolve the residue in water, add a few drops of dilute sulphuric acid, then a little weak solution of iodide of potassium, and, lastly, some mucilage of starch; the deep-blue "iodide of starch" is produced. $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$. Repeat this experiment, using nitrate of potassium instead of nitrite; no blue colour is produced.

Test for Nitrites in Water.—This liberation of iodine by nitrites and not by nitrates is a reaction of considerable value in searching for nitrites in ordinary drinking waters, the occurrence of such salts, except in very deep-seated springs, being held to indicate the presence of nitrogenous organic matter in a state of oxidation or decay. The sulphuric acid used in the operation must be pure, and the iodide of potassium free from iodate. If much organic matter is present, however, the nitric acid liberated by the sulphuric may be reduced to nitrous acid. It is perhaps best, therefore, to add acetic acid, and (Fresenius) distil over 10 or 20 per cent. of the water and apply the test to this distillate. Very dilute solutions of nitrous acid may thus be distilled without the slightest decomposition.

Commercial Nitrous Acid.—The liquid commonly termed in pharmacy "nitrous acid," is simply nitric acid impure from the presence of nitrous acid.

Other nitrites used in medicine are nitrites of organic basylous radicals; nitrite of ethyl ($C_2H_5NO_2$), or nitrous ether, is the most important constituent of *Spiritus Ætheris Nitrosi*, B.P. (*vide* Index). Nitrite of amyl ($C_5H_{11}NO_2$) is also official (*Amyl Nitris*, B.P.). Nitrite of ammonium, on being heated, yields pure nitrogen gas:—$NH_4NO_2 = 2H_2O + N_2$.

Nitrite of Sodium, $NaNO_2$, (*Sodii Nitris*, B.P.). It yields ruddy nitrous fumes on the addition of sulphuric acid, and gives the usual deep brown colour with sulphate of iron (p. 337).—"One grain of the salt dissolved in water and introduced into a nitrometer and tested with iodide of potassium and diluted sulphuric acid, should liberate not less than 325 grain-measures of nitric oxide, the gas being almost completely absorbed by strong solution of sulphate of iron; corresponding to not less than 95 per cent. of nitrite of sodium. The aqueous solution of the salt must not give more than traces of precipitate with solution of chloride of calcium," showing absence of any important proportion of oxalates.

OPHELIC ACID ($C_{13}H_{20}O_{10}$).—This is one of the principles to which the herb *Ophelia chirata*, or Chiretta (*Chirata*, B.P.), owes its bitterness. It is an amorphous yellow body. Another is *Chiratin* ($C_{26}H_{48}O_{15}$), decomposable by hydrochloric acid into *Chiratogenin* ($C_{13}H_{24}O_3$) and ophelic acid (Höhn).

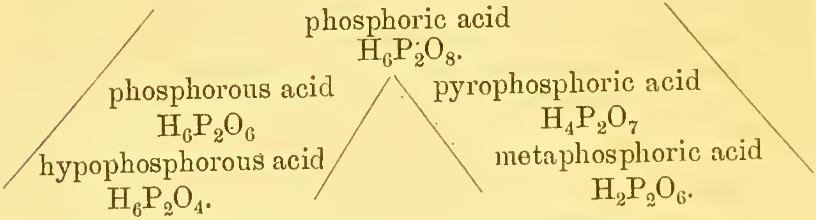
PHOSPHOROUS ACID (H_3PO_3, or $P(OH)_3$, or H_2PHO_3).—The three acids of phosphorus, namely, phosphoric acid (H_3PO_4), phosphorous acid (H_2PHO_3), and hypophosphorous acid (HPH_2O_2), differ from each other in the proportion of oxygen, the molecules containing four, three, and two atoms respectively. In constitution they differ by the hypothetical phosphoric radical or grouping being trivalent, the phosphorous radical bivalent, and the hypophosphorous radical univalent. These three acids and corresponding salts must not be confounded with pyrophosphoric and metaphosphoric acids and salts: the former are acids of phosphorus; the latter varieties of phosphoric acid: the former differ in proportion of oxygen; the latter by the elements of water:—

Acids of phosphorus.	*Varieties of phosphoric acid.*
H_3PO_4 phosphoric acid.	H_3PO_4 (ortho)phosphoric acid.
H_2PHO_3 phosphorous acid.	$H_4P_2O_7$ pyrophosphoric acid.
HPH_2O_2 hypophosphorous acid.	HPO_3 metaphosphoric acid.

When hypophosphorous acid is exposed to the air, oxygen is absorbed and phosphorous acid results; by prolonged exposure more oxygen is absorbed and phosphoric acid is obtained. When phosphoric acid, or rather, for distinction, orthophosphoric acid, is heated, every two molecules yield the elements of a molecule of water, and pyrophosphoric acid results; by prolonged exposure to heat more water is evolved, and metaphosphoric acid is obtained. These differences will be further evident if the formulæ be written empirically, nearly all being doubled, thus:—

$H_6P_2O_4$	hypophosphorous acid.
$H_6P_2O_6$	phosphorous acid.
$H_6P_2O_8$	phosphoric acid, or orthophosphoric acid.
$H_4P_2O_7$	pyrophosphoric acid.
$H_2P_2O_6$	metaphosphoric acid.

Or thus:—



From the central compound, ordinary phosphoric acid, the acids of phosphorus differ by regularly diminishing proportions of the element oxygen, the varieties of phosphoric acid by regularly diminishing proportions of the elements of water.

Prepare phosphorous acid by exposing a moist stick of phosphorus to the air; a thin stream of heavy white vapour falls, which contains the acid in question. A simple method of collection is to place the stick in an old test-tube having a hole in the bottom, to support this tube by a funnel or otherwise, the neck of the funnel being supported in a bottle, test-glass, or tube, at the bottom of which is a little water. Or phosphorous oxide, P_4O_6, may first be obtained by heating phosphorus in a tube, through which a slow current of air is drawn, condensing the fumes in a U-tube surrounded by a freezing mixture, and then decomposing the oxide by water. Or chlorine is passed through phosphorus melted under water;—$PCl_3 + 3H_2O = P(HO)_3 + 3HCl$. Having collected some phosphorous acid, apply the various tests already alluded to under *Hypophosphorous Acid*, first carefully neutralizing the phosphorous acid by an alkali. The means by which the varieties of phosphoric acid are distinguished have been given under *Metaphosphoric Acid.*

Other soluble phosphites are prepared by neutralizing phosphorous acid with alkalies, and the insoluble phosphites by double decomposition.

Associated with phosphorous acid prepared as above stated, there is said to be an acid of the formula H_2PO_3 termed *hypophosphoric acid.* Its anhydride would be P_2O_4.

It is interesting to note that during the oxidation of phosphorus in moist air, not only are phosphoric, hypophosphoric, and phosphorous acids formed, but also ozone (O_3), peroxide of hydrogen (H_2O_2), and a small quantity of nitrate of ammonium (NH_4NO_3).

PYROGALLIC ACID.—*See* TANNIC ACID.

PYROPHOSPHORIC ACID ($H_4P_2O_7$) AND OTHER PYROPHOSPHATES.—Heat ordinary phosphate of sodium (Na_2HPO_4, $12H_2O$) in a crucible; water of crystallization is first evolved, and dry phosphate (Na_2HPO_4) remains. Further heat to redness; two molecules yield one of water, while a salt having new properties is obtained:—$2Na_2HPO_4 - H_2O = Na_4P_2O_7$. It is termed pyrophosphate of sodium, in allusion to its origin (πῦρ, *pūr*, fire). From its solution in water it may be obtained in prismatic crystals ($Na_4P_2O_7$, $10H_2O$). Phosphoric acid itself is similarly affected by heat:—$2H_3PO_4 - H_2O = H_4P_2O_7$ (pyrophosphoric acid), though metaphosphoric acid is also formed. Other pyrophosphates are similarly produced; or by double decomposition and precipitation, or by neutralizing pyrophosphoric acid by an oxide, hydrate, or carbonate.

Tests.—To solution of a pyrophosphate add solution of nitrate of silver; a dense white precipitate falls (pyrophosphate of silver, $Ag_4P_2O_7$) differing much in appearance from the white gelatinous metaphosphate of silver or the yellow orthophosphate. To pyrophosphoric acid, or to a pyrophosphate mixed with acetic acid, add an aqueous solution of albumen (white of egg); no precipitate occurs. Metaphosphoric acid, it will be remembered, gives a white precipitate with albumen.

QUESTIONS AND EXERCISES.

What are the sources of lactic acid?—How is lactic acid usually prepared?—Name some of the plants in which malic acid is found.—Whence is meconic acid derived?—By what process may meconic acid be isolated? Which is the best test for the meconic radical?—Distinguish meconates from sulphocyanates.—Give the mode of manufacture of hypophosphites. How is phosphoretted hydrogen prepared?—By what ready method may metaphosphoric acid be obtained for experimental purposes?—Name the tests for metaphosphates.—How may meta- or pyro-phosphoric acid be converted into orthophosphoric acid?—Describe the preparation of phosphorous acid.—State the relations of the acids of phosphorus to each other.—How are the pyrophosphates prepared?—Define, by formulæ, metaphosphates, pyrophosphates, orthophosphates, phosphites, and hypophosphites.—Mention the tests by which meta-, pyro-, and orthophosphates are analytically distinguished.—How are hypophosphites and phosphites detected?

SILICIC ACID (H_4SiO_4) AND OTHER SILICATES.—Silicates of various kinds are among the commonest of minerals. The various *clays* are aluminium silicates; the volcanic substance termed *pumice-stone* is a porous silicate of aluminium and of alkali-metals or of alkaline-earth metals; *meerschaum* is an acid silicate of magnesium; the ordinary *sandstones* are chiefly silica; *sand, flint, quartz, agate, chalcedony,* and *opal* are silicic anhydride or *silica* (SiO_2). *Tripoli*, a polishing powder now found in many other countries than Tripoli, and consisting of infusorial skeletons, is nearly pure silica. *Bath* *brick*, used in knife-polishing, is a silico-calcareous deposit, found in the estuary at Bridgwater and other places. *Tourmalines*, plates of which, cut parallel to the axis of a crystal, are used as polarisers or analysers in microscopy are all silicates of aluminium with varying silicates of iron, copper manganese, etc. *Asbestos* or *amianth* is a fibrous silicate of calcium and magnesium, the length of the fibres being from less than one inch to five feet. A single silk-like fibre can easily be fused, but even in very small masses, and for all practical purposes, asbestos is infusible, and, of course, incombustible. It is also a bad conductor of heat. It is already largely used in packing piston rods and joints, and for steam apparatus generally ; as a covering for boilers to prevent loss of heat by radiation; and for so lining ceilings, floors, and other partitions as to render rooms, etc., fireproof. Artificial acid, and therefore insoluble, silicates are familiar under the forms of *glass* and *earthenware*. Common English window-glass is usually silicate of calcium, sodium, and aluminium ; French glass, silicate of calcium and sodium ; Bohemian, chiefly silicate of potassium and calcium, English flint or crystal-glass for ornamental, table, and optical purposes, is mainly silicate of potassium and lead. Earthenware is mostly silicate of aluminium (clay), with more or less of the more fusible silicates, namely, those of calcium, sodium and potassium, and in the commoner forms, silicate of iron. The various kinds of *porcelain* (China, Sèvres, Meissen, Berlin, English), *Wedgwood-ware*, and *stoneware* are varieties of earthenware. *Kaolin*, or *China clay*, which is disintegrated *felspar*, not more common in China than in Devonshire and Cornwall, is the clay which yields the finest translucent porcelain. *Crucibles*, *bricks*, and *tiles* are clay-silicates. *Fire-clay* contains excess of silica and very small proportions of the fusible silicates, hence its refractory character. *Mortar* is essentially silicate of calcium. *Portland*, *Roman*, and other "hydraulic" *cements** are silicates of calcium with more or less of aluminium.

Mix together a few grains of powdered flint or sand with about five or six times its weight of carbonate of sodium and an equal quantity of carbonate of potassium, and fuse a little of the mixture on platinum foil in the blowpipe-flame; the product is an alkaline and therefore soluble silicate, a kind of *soluble glass*. Boil the foil in water for a few minutes; filter; to a portion add excess of hydrochloric acid, evaporate the solution to dryness, and again boil the residue in water and acid; oxide of silicon, silicic anhydride, or *silica* (SiO_2) remains as a light, flaky, insoluble powder.

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* For an article on "Cements" generally, *see Pharmaceutical Journal* for April 17th, 1880.

The *soluble glass* or *glass liquor* of trade commonly contains 10 or 12 per cent. of soda (NaHO) to 20 or 25 per. cent. of silica (SiO_2).

The foregoing operation constitutes the *test* for silicates. By fusion with alkali the silicate is decomposed, and a soluble alkaline silicate formed. On addition of acid, silicic acid (H_4SiO_4) is set free, but remains in solution if the fluid is not too strong. The heat subsequently applied eliminates water and reduces the silicic acid to silica (SiO_2), which is insoluble in water or acid. By the addition of hydrochloric acid to soluble glass, and removal of the resulting alkaline chloride and excess of hydrochloric acid by dialysis (a process to be subsequently described), a pure aqueous solution of silicic acid may be obtained; it readily changes into a gelatinous mass of silicic acid. Possibly some of the natural crystallized varieties of silica may have been obtained from the silica contained in such an aqueous solution, nearly all waters yielding a small quantity of silica when treated as above described.

A variety of silicic acid (H_2SiO_3), sometimes termed *dibasic* to distinguish it from the normal or *tetrabasic* acid (H_4SiO_4), results when the aqueous solution of the latter is evaporated *in vacuo*.

Siliciuretted hydrogen, or hydrido of silicon (SiH_4), is a spontaneously inflammable gas formed on treating silicide of magnesium with hydrochloric acid. It is tho analogue of light carburetted hydrogon or mothane (CH_4). A liquid chloride of silicon ($SiCl_4$) analogous to totrachlorido of carbon (CCl_4) and a gaseous fluorido (SiF_4) also exist.

Many other analogies aro tracoable between the elements silicon and carbon, including, perhaps, boron, especially amongst their organic compounds.

SUCCINIC ACID ($H_2C_4H_4O_4$).—Ambor (*Succinum*) is a resin usually occurring in association with coal and lignite. From the fact that fragments of coniferous fruit are frequently found in amber, and impressions of bark on its surface, it is considered to have been an exudation from a species of *Pinus* now probably extinct. Heated in a retort, amber yields, first, a sour aqueous liquid containing acetic acid and another characteristic body appropriately termed *succinic acid;* secondly, a volatile liquid known as *oil of amber*, resembling the oil yielded by most resinous substances under similar circumstances; and, thirdly, a pitchy residue allied to asphalt. The succinic acid is a normal constituent of the amber, the acetic acid is produced during distillation. Succinic acid has also been found in wormwood, in several pine-resins, and in certain animal fluids, such as those of hydatid cysts and hydrocele. It may be obtained artificially from butyric, stearic, or margaric acid by oxidation. Tartaric, malic, and succinic acids are also convertible the one into the other.

Succinates are neutral ($R'_2C_4H_4O_4$) and acid ($R'HC_4H_4O_4$); a double succinate of potassium and hydrogen ($KHC_4H_4O_4$, $H_2C_4H_4O_4$, H_2O), analogous to the superacid oxalate, salt of sorrel, also exists. Soluble succinates give a bulky brown precipitate with neutral ferric chloride, only less voluminous than ferric benzoate; a white precipitate with acetate of lead, soluble in excess of either reagent; with nitrate of silver a white precipitate after a time; with chloride of barium no precipitate at first, but a white one (succinate of barium) on the addition of ammonia and alcohol. Succinates are distinguished from benzoates by the last-named reaction, and by not yielding a precipitate on the addition of acids (*vide* p. 398).

SULPHOCYANIC ACID (HCNS) AND OTHER SULPHOCYANATES.—Boil together sulphur and solution of cyanide of potassium; solution of sulphocyanate of potassium (KCNS) is formed. Warm the liquid, add hydrochloric acid till it faintly reddens litmus-paper, and filter; any sulphide of potassium is thus decomposed, and the solution may then be used for the following reactions. The salt readily crystallizes.

Tests.—To a small portion of the solution add a ferric salt (Fe_2Cl_6); a deep blood-red solution (ferric sulphocyanate) is formed. To a portion of the red liquid add a little hydrochloric acid; the colour is not discharged (meconate of iron, a salt of similar tint, is decomposed by hydrochloric acid). In the acid liquid place a fragment or two of zinc; sulphuretted hydrogen is evolved, and the red colour disappears.

To another portion of the ferric sulphocyanate add solution of corrosive sublimate; the colour is at once discharged. (Ferric meconate is unaffected by corrosive sublimate). The ferric is the best test of the presence of a sulphocyanate; and indirectly is also a good test of the presence of hydrocyanic acid or cyanogen (*see* p. 329). Solutions of pure ferrous salts are not coloured by the solution of sulphocyanate. Red ferric acetate is decomposed by ebullition. Neither the ferric acetate nor the meconate yield their colour to ether; but, on shaking ferric sulphocyanate solutions with ether, the latter takes up the salt and becomes of a purple colour.

To solution of a sulphocyanate add solution of mercuric nitrate; mercuric sulphocyanate is precipitated as a white powder.

Pharaoh's Serpents.—Mercuric sulphocyanate, thoroughly washed and made up into little cones, forms the toy termed Pharaoh's serpent. It readily burns when ignited, the chief product being a light solid matter (mellon, C_9N_{13}, and melam, $C_3H_6N_6$), which issues from the cone in a snake-like coil of extraordinary length. The other products are mercuric sulphide (of which part remains in the snake and part is volatilized), nitrogen, sulphurous and carbonic acid gases, and vapour of metallic mercury. (For details concerning the economical manufacture of sulphocyanates, *see Pharmaceutical Journal*, 2nd series, vol. vii. p. 581, and p. 152.)

The sulphocyanic radical (CNS) is often termed sulphocyanogen (Scy), and its compounds regarded as *sulphocyanides*. Saliva contains sulphocyanates.

TANNIC ACID OR TANNIN. *Digallic acid.* ($C_{14}H_{10}O_9$).—This is a very common astringent constituent of plants, but is contained in largest quantity in galls (excrescences on the oak formed by the puncture and deposited ova of an insect). English galls contain from 14 to 28 per cent. of tannic acid;

Aleppo galls (*Galla*, B.P.) 25 to 65. (*Acidum Tannicum*, B.P.).
Gallotanic acid...$C_6H_2(OH)_3CO{\cdot}O{\cdot}C_6H_2(OH)_2COOH$.
Gallic acid (p. 426)....$C_6H_2(OH)_3COOH$.

Process.—" Expose powdered galls [about an ounce is sufficient for the purpose of study] to a damp atmosphere for two or three days, and afterwards add sufficient ether to form a soft paste. Let this stand in a well-closed vessel for twenty-four hours, then, having quickly enveloped it in a linen cloth, submit it to strong pressure, so as to separate the liquid portion, which contains the bulk of the tannin in solution. Reduce the pressed cake to powder, mix it with sufficient ether, to which one-sixteenth of its bulk of water has been added, to form again a soft paste, and press this as before. Mix the expressed liquids, and expose the mixture to spontaneous evaporation until, by the aid subsequently of a little heat, it has acquired the consistence of a soft extract; then place it on earthen plates or dishes, and dry it in a hot-air chamber at a temperature not exceeding 212° F."

The resulting tannic acid occurs in " pale yellow vesicular masses, or thin glistening scales, with a strongly astringent taste and an acid reaction, readily soluble in water, and rectified spirit, very sparingly soluble in pure ether, though soluble in the ethereal fluid used in the foregoing process—a fluid which is really a mixture of true ether, water, and alcohol (both the latter contained in the common " ether ") and a little added water also.

Medicinal Uses.—Tannic acid is very soluble in water, and in this form is usually administered in medicine. Its official preparations are *Glycerinum Acidi Tannici*, *Suppositoria Acidi Tannici*, *Suppositoria Acidi Tannici cum Sapone*, and *Trochisci Acidi Tannici.*

Tests.—To an aqueous solution of tannic acid add aqueous solution of gelatine ; a yellowish-white flocculent compound of the two substances is precipitated.

Tanning.—The above reaction also serves to explain the chemical principle involved in *tanning*—the operation of converting skin into leather. In that process the skin is soaked in infusion of oak-bark (*Quercûs Cortex*, B.P.), the tannic acid of which, uniting with the gelatinous tissues of the skin, yields a compound very well represented by the above precipitate. The outer bark of the oak contains little or no tannic acid, and is commonly shaved off from the pieces of bark which are large enough to handle; useless colouring matter is thus also rejected. Other infusions and extracts besides that of oak-bark (chiefly catechu, sumach, and valonia) are largely used by tanners; if used alone, these act too quickly, and give a harsh, hard, less durable leather. The tannic acid of these preparations is probably slightly different from that of oak-bark.

To an aqueous solution of tannic acid add a neutral solution of a ferric salt; dark bluish-black tannate of iron is slowly precipitated. This is an excellent test for the presence of tannic acid in vegetable infusions. The precipitate is the basis of nearly all black *writing-ink*. Ferrous salts give at first only a slight reaction with tannic acid; but the liquid gradually darkens: characters written with a liquid of this kind of proper strength become quite black in a few hours, and are very permanent.

To an aqueous solution of tannic acid add solution of tartar-emetic; tannate of antimony is precipitated. This reaction and that with gelatine are useful in the quantitative estimation of the amount of tannic acid in various substances, the separation of the tannate of gelatine being much promoted by previously adding some heavy neutral powder, such as sulphate of barium, and well stirring while adding the gelatine.

Tannic acid, as it occurs in oak-bark, is said to be a glucoside; that is, like several other substances, it yields glucose (grape-sugar) when boiled with dilute sulphuric or hydrochloric acid, the other product being gallic acid. Possibly, however, the sugar is not a necessary constituent of the tannin, certainly not of all of them.

Catechu (*Catechu*, B.P.), *Gambier*, or *Terra Japonica*, an extract of the *Uncaria Gambier;* as well as the true *Catechu*, *Cutch*, or *Terra Japonica*, an extract from the *Acacia Catechu* (*Catechu nigrum*, P.I.) and *A. Suma ; East Indian Kino* (*Kino*, B.P.), from the *Pterocarpus marsupium;* also *Bengal* or *Butea Kino*, from the *Palas* or *Dhak* tree, *Butea frondosa* (*Buteæ gummi vel Kino Bengalensis*, P.I.) ; Botany Bay or Australian kinos from various species of *Eucalyptus* or Blue Gum trees ; and some other vegetable products—contain a variety of tannic acid (*mimotannic acid*), which gives a greenish precipitate with neutral solutions of ferric salts. According to Paul and Kingzett it yields, when decomposed, unfermentable sugar, and an acid different to ordinary gallic acid. Catechu and Gambier also contain *catechuic acid* or *catechin*, $C_{13}H_{12}O_5$, a body occurring in minute colourless acicular crystals, and, like mimotannic acid, affording a green precipitate with ferric salts.

Bael fruit (*Belæ Fructus*, B.P.), from the *Ægle Marmelos*, is said to owe its power as a remedy for dysentery and diarrhœa to a variety of tannic acid ; but this is questionable. The rind of the fruit of the *pomegranate* (*Punica granatum*) (*Granati Cortex*, P.I.) contains tannic acid. The astringency of Pomegranate-root Bark (*Granati Radicis Cortex*, B.P. and P.I.) is due to a tannic acid (its anthelmintic properties probably to a resinoid matter, or possibly to what Tanret states to be a liquid alkaloid, *pelletierine*, $C_{16}H_{30}N_2O_2$). A tannic acid also probably gives the astringency to logwood (*Hæmatoxyli Lignum*, B.P.). *Rhatany*-root Bark (*Krameriæ Radix*, B.P.) contains about 20 per cent. of tannic acid, its active astringent principle ; rhubarb-root about 9 per cent. *Bearberry* leaves (*Uvæ Ursi Folia*, B.P.) owe most of their therapeutic power to about 35 per cent. of tannic acid. (The cause of their influence on the kidneys is not yet traced). They also contain *arbutin*, a crystalline glucoside. *Larch-bark* (*Laricis Cortex*, B.P.), the inner bark of *Pinus Larix* or *Larix Europæa*, contains, according to Stonhouse, a considerable amount of a tannic acid giving olive-green precipitates with salts of iron, and *larixin* and *larixinic acid* ($C_{10}H_{10}O_5$), a somewhat bitter substance. *Areca nuts* or *Betel nuts*, from the Areca Palm (*Areca Catechu*), besides the alkaloid *arekane* (Bombelon), contain a very active alkaloid, *arecoline*, $C_8H_{13}NO_2$ (Jahns), said to be the vormifugal principle ; *arecaine*, an inert alkaloid (Jahns), and, according to

Flückiger and Hanbury, about 16 per cent. of "tannic matter." The extract of the fruit of *Gab* or *Diospyros embryopteris* (*Diospyri Fructus*, P.I.) is a powerful astringent containing tannic acid. The rhizome of *Geranium maculatum*, *Spotted Cranesbill*, or *Alum-root*, contains both tannic and gallic acids.

Gallic Acid ($H_3C_7H_3O_5$, H_2O) (*Acidum Gallicum*, B.P.) occurs in small quantity in oak-galls and other vegetable substances, but is always prepared from tannic acid. Gallic acid forms slender acicular, fawn-coloured crystals, soluble in 118 times their weight of cold or three of boiling water, freely in spirit, sparingly in ether.

"Boil one part of coarsely powdered galls with four fluid parts of diluted sulphuric acid for half an hour, then strain through calico while hot; collect the crystals that are deposited on cooling, and purify these with animal charcoal and repeated crystallization."

Test.—To an aqueous solution of gallic acid add a neutral solution of a ferric salt; a bluish-black precipitate of gallate of iron falls, similar in appearance to tannate of iron. Ferrous salts also are blackened by gallic acid. To more of the solution add an aqueous solution of gelatine; no precipitate occurs. By the latter test gallic is distinguished from tannic acid.

Pyrogallic acid or *pyrogallol*, $C_6H_3(OH)_3$.—This substance sublimes in light feathery crystals when gallic acid is heated. Or it may be formed by heating gallic acid with 3 or 4 times its weight of glycerine to a temperature of 190° or 200° C. for a short time, until carbonic acid ceases to be evolved. Longer heating at lower temperatures is not equally effective, and below 100° C. probably no pyrogallol is produced (Thorpe). To an aqueous solution add a neutral solution of a ferric salt; a red colour is produced. To another portion add a ferrous salt; a deep-blue colour results.

Test for the three acids.—To three separate small quantities of milk of lime in test-tubes add, respectively, tannic, gallic and pyrogallic acids; the first slowly turns brown, the second more rapidly, while the pyrogallic mixture at once assumes a beautiful purplish-red colour changing to brown. These reactions are characteristic; they are accompanied by absorption of oxygen from the air.

Use of Pyrogallic Acid in Gas-analysis.—A mixture of pyrogallic acid and solution of potash absorbs oxygen with such rapidity and completeness that a strong solution of each, passed up successively by a pipette into a graduated tube containing air or other gas, form an excellent means of estimating free oxygen. The value of this method may be roughly proved by pouring a small quantity of each solution into a phial, immediately and firmly closing its mouth with a cork, thoroughly shaking the mixture, and then removing the cork under water: the water rushes in and occupies about one-fifth of the previous volume of air, indicating that the atmosphere contains one-fifth of its bulk of oxygen. The small amount of carbonic acid gas present in the air is also absorbed by the alkaline liquid; in delicate experiments this should be removed by the alkali before the addition of pyrogallic acid.

URIC ACID ($H_2C_5H_2N_4O_3$) AND OTHER URATES.—Acidulate a few ounces of human urine with hydrochloric acid, and set aside for twenty-four hours: a few minute crystals of uric acid will be found adhering to the sides and bottom of the vessel and floating on the surface of the liquid.

Microscopical Test.—Remove some of the floating particles by a slip of glass, and examine by a powerful lens or microscope; the chief portion will be found to be in yellowish semi-transparent crystals, more or less square, two of the sides of which are even and two very jagged; but other forms are common. (*See* the lithographs in the section on Urinary Sediments.)

Chemical Test.—Collect more of the deposit, place in a watch-glass or small white evaporating-dish, remove adherent moisture by a piece of blotting- or filter-paper, add a drop or two of strong nitric acid, and evaporate to dryness; the residue will be red. When the dish is cold, add a drop of solution of ammonia; a purplish-crimson colour results. The colour is deepened on the addition of a drop of solution of potash.

Notes.—Uric acid (or lithic acid) and urates (or lithates) of sodium, potassium, calcium, and ammonium are common constituents of animal excretions. Human urine contains about one part of urate (usually urate of sodium) in 1,000. When more than this is present, the urate is often deposited as a sediment in the excreted urine, either at once, or after standing a short time. Uric acid or other urate is also occasionally deposited before leaving the bladder, and, slowly accumulating there, forms a common variety of urinary calculus.——Some urates are not definitely crystalline; but, when treated with dilute nitric acid or a drop of solution of potash and then a drop or two of acetic acid, jagged microscopic crystals of uric acid are usually formed.—All urates yield the crimson colour when treated as above described.—This colour is due to a definite substance, *murexid* ($C_8H_8N_6O_6$) (from the *murex*, a shell-fish of similar tint, and from which the ancient and highly valued purple dye seems to have been prepared); and the test is known as the *murexid* test. The formation of murexid is due to the action of ammonia on *alloxan* ($C_4H_2N_2O_4$, $4H_2O$) and other white crystalline products of the oxidation of uric acid by nitric acid. Murexid is a good dye; it may be prepared from *guano* (the excrement of sea-fowl), which contains a large quantity of urate of ammonium.—The excrement of the serpent is almost pure ammonium urate.

Uric acid and the urates will again be alluded to in connection with the subject of morbid urine.

Constitution of Uric Acid.—The physiological and pathological importance of uric acid has obtained for it great attention from chemists, a knowledge of its constitution being rightly regarded as amongst the most prominent of chemical desiderata. For accounts of what has been done in this direction in recent years, students of organic chemistry may consult the *Pharmaceutical Journal*, 3rd Series, vol. xiv., p. 771; vol. xv., pp. 119 and 411; and vol. xviii., p. 69. See also page 464.

Valerianic Acid, or Valeric Acid ($HC_5H_9O_2$), and other Valerianates.—In a test-tube place a few drops of amylic alcohol (fousel-oil) with a little dilute sulphuric acid and a grain or two of red chromate of potassium, cork the tube, set aside for a few hours, and then heat the mixture; valerianic acid, of characteristic valerian-like odour, is evolved.

Valerianic acid occurs in valerian-root in association with the essential oil from which it is apparently derived (*vide* Index), but is usually prepared artificially, by the foregoing process, from amylic alcohol, to which it bears the same relation as acetic acid does to common alcohol:—

$$C_2H_5HO + O_2 = HC_2H_3O_2 + H_2O.$$
$$C_5H_{11}HO + O_2 = HC_5H_9O_2 + H_2O.$$

Valerianate of Sodium ($NaC_5H_9O_2$) (*Sodii Valerianas*, B.P.), the old Valerianate of Soda, is prepared from the valerianic acid and valerianate of amyl obtained on distilling the mixture of amylic alcohol (4 fl. oz.), sulphuric acid (6½ fl. oz. with 10 of water), and red chromate of potassium (9 oz. in 70 of water). The mixture should stand for several hours before heat is applied.

$$\underset{\text{Red chromate of potassium.}}{2(K_2CrO_4, CrO_3)} + \underset{\text{Sulphuric acid.}}{8H_2SO_4} = \underset{\text{Sulphate of potassium and chromium (chrome alum).}}{2(K_2SO_4, Cr_2 3SO_4)} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Oxygen.}}{3O_2}$$

$$\underset{\text{Amylic alcohol.}}{C_5H_{11}HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Valerianic acid.}}{HC_5H_9O_2} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Amylic alcohol.}}{2C_5H_{11}HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Valerianate of amyl.}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Water.}}{2H_2O.}$$

The distillate (70 or 80 oz.) is saturated with soda, which not only yields valerianate of sodium with the free valerianic acid, but decomposes the valerianate of amyl produced at the same time, more valerianate of sodium being formed and some amylic alcohol set free, according to the following equations:—

$$\underset{\text{Valerianic acid.}}{HC_5H_9O_2} + \underset{\text{Soda.}}{NaHO} = \underset{\text{Valerianate of sodium.}}{NaC_5H_9O_2} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Valerianate of amyl.}}{C_5H_{11}C_5H_9O_2} + \underset{\text{Soda.}}{NaHO} = \underset{\text{Valerianate of sodium.}}{NaC_5H_9O_2} + \underset{\text{Amylic alcohol.}}{C_5H_{11}HO}$$

From the solution of valerianate of sodium (which should be made neutral to test-paper by careful addition of soda solution) the solid white salt is obtained by evaporation to dryness and cautious fusion of the residue. The mass obtained on cooling should be broken up and kept in a well-closed bottle. It should be entirely soluble in spirit.

Other Valerianates, as valerianate of zinc (*Zinci Valerianas*, B.P.) and ferric valerianate ($Fe_26C_5H_9O_2$), may be made by double decomposition of valerianate of sodium with the sulphate or other salt of the metal the valerianate of which is desired, the new valerianate either precipitating or crystallizing out. A hot solution of sulphate of zinc ($5\frac{3}{4}$ parts) and valerianate of sodium (5 parts) in water (40 parts) gives a crop of crystals of valerianate of zinc on cooling.

Tests.—Heated with diluted sulphuric acid, valerianates of the metals give a highly characteristic smell (valerianic acid).

The amylic alcohol ($C_5H_{11}HO$) from which valerianates are prepared may contain the next lower homologue, *butylic alcohol* (C_4H_9HO) (*vide* "Homology" in the Index). This, during oxidation, will be converted into *butyric acid* ($HC_4H_7O_2$), the next lower homologue of valerianic acid ($HC_5H_9O_2$), and hence the various valerianates be contaminated by some *butyrates*. These are detected by distillation with diluted sulphuric acid and addition of solution of acetate of copper to the distillate, which at once becomes turbid if butyric acid be present. In this reaction valerianic and butyric acids are produced by double decomposition of the valerianate and butyrate by the sulphuric acid, and distil over on the application of heat. On the addition of acetate of copper ($Cu2C_2H_3O_2$) butyrate of copper ($Cu2C_4H_7O_2, H_2O$)

is formed, and, being almost insoluble in water, is at once precipitated, or remains suspended, giving a bluish-white opalescent liquid. Valerianate of copper ($Cu2C_5H_9O_2$) is also formed after some time, but is far more soluble than the butyrate, and only slowly collects in the form of greenish oily drops, which gradually pass into greenish-blue hydrous crystalline valerianate of copper (Larocque and Huralt).

VANILLIC ACID ($HC_8H_7O_3$) or VANILLIN ($C_8H_8O_3$) or METHYL-PROTOCATECHUIC ALDEHYDE ($C_7H_5CH_3O_3$), is the body to which is due the odour and flavour of vanilla. It also occurs in Siam benzoin, *Rosa canina*, etc. The white crystals commonly found on vanilla (the prepared unripe pods of *Vanilla planifolia*), previously termed *vanillin*, were found by Carles to be a weak acid. It occurs in vanilla to the extent of from 1½ to 3 per cent. Vanillin has recent years been prepared artificially by Tiemann and Haarman from coniferin, a glucoside existing in the sapwood of pines. The body remaining after the removal of glucose from coniferin, or, indeed, coniferin itself, by action of a mixture of red chromate of potassium and sulphuric acid, yields the vanillin. It also may be obtained by a series of reactions starting from that of carbonic acid on carbolate of potassium; also from the eugenol of oil of cloves. By action of hydrochloric acid, vanillin yields chloride of methyl and protocatechuic aldehyd. Such reactions will be better understood when the pupil has studied succeeding sections on what is commonly termed *Organic Chemistry*. Artificial vanilla is less stable that natural vanillin, perhaps because with the latter is associated a preservative resin.

QUESTIONS AND EXERCISES.

What is the constitution of nitrites?—Mention a test for nitrites in potable waters.—Which nitrites are official?—Give the names of some natural and artificial silicates.—What is "soluble glass"?—Distinguish between silica and silicic acid.—How are silicates detected?—What is the quantivalence of silicon?—Mention the sources, formulæ, and analytical reactions of succinates—State the mode of manufacture and tests of sulphocyanates.—What proportion of tannic acid is contained in galls?—Describe the official process for the preparation of tannic acid.—Explain the chemistry of "tanning."—Enumerate the tests for tannic acid.—What is the assumed constitution of tannic acid?—Mention official substances other than galls whose astringency is due to tannic acid.—How is gallic acid prepared?—By what reaction is gallic distinguished from tannic acid?—Mention the characteristic properties of pyrogallic acid.—Explain the murexid test for uric acid.—Describe the artificial preparation of valerianic acid and other valerianates, giving diagrams or equations.—What is the formula of valerianic acid?—How are butyrates detected in presence of valerianates?

DETECTION OF THE ACIDULOUS RADICALS OF SALTS SOLUBLE IN WATER.

Analytical operations may now be resumed, the detection of acidulous radicals being practised for two or three days, and then full analyses made, both for basylous and acidulous radicals. To this end a few compounds of stated metals (potassium, sodium, or ammonium) should be placed in the hands of the practical student for examination according to the following paragraphs and Tables. Mixtures in which both basylous and acidulous radicals may be sought should then be analysed.

In examining salts soluble in water, and concerning which no general information is obtainable, search must first be made for any basylous radicals by the appropriate methods (*vide* pp. 257 or 298–303). Certain metals having been thus detected, a little reflection on the character of their salts will at once indicate what acidulous radicals may be, and what cannot be, present. Thus, for instance, if the substance under examination is freely soluble in water, and lead is found, only the nitric and acetic radicals need be sought, none other of the lead salts than nitrate or acetate being freely soluble in water. Moreover the salt is more likely to be acetate than nitrate of lead, for two reasons: the former is more soluble than the latter, and is by far the commoner salt of the two. Medical and pharmaceutical students have probably, in dispensing, already learnt much concerning the solubility of salts, and whether a salt is rarely employed or is in common use. And although but little dependence can be placed on the chances of a salt being present or absent according to its rarity, still the point may have its proper weight. If, in a mixture of salts, ammonium, potassium, and magnesium have been found associated with the sulphuric, nitric, and hydrochloric radicals, and we are asked how we suppose these bodies may exist in the mixture, it is far more in accordance with common sense to suggest that sal-ammoniac, nitre, and epsom salt were originally mixed together, than to suppose any other possible combination. Such appeals to experience regarding the solubility or rarity of salts cannot be made by any one not previously acquainted, or insufficiently acquainted, with the characters of salts; in such cases the relation of a salt to water and acids can be ascertained by referring to the following Table (p. 436) of the solubility or insolubility of about five hundred of the common and rarer salts met with in chemical operations.

The opposite course to the above (namely, to ascertain what acidulous radicals are present in a mixture, and then to appeal to experience to tell what basylous radicals may be and what cannot be present) is impracticable; for acidulous radicals cannot be separated out, one after the other, from one and the same quantity of substance by a similar treatment to that already given for basylous radicals. Indeed such a sifting of acidulous radicals could scarcely be accomplished at all, or only by a vast deal of labour. The basylous radicals must therefore first be detected.

Even when the basylous radicals have been found, the acidulous radicals which may be present must be sought for singly, the only additional aid which can be brought in being the action of sulphuric acid, a barium salt, a calcium salt, nitrate of silver, and ferric chloride on *separate* small portions of the solution under examination, as detailed in the second of the following Tables.

Practical Analysis.

Commence the analysis of an aqueous solution of a salt or salts, the basylous radicals in which are known, by writing out a list of the acidulous radicals which may be, or, if more convenient, of those which cannot be present. To this end, consult the following Table (p. 436) of the solubility of salts in water. Look for the name of the metal of the salt in the vertical column; the letters S and I indicate which salts are soluble and which insoluble in water, an asterisk attached to the S meaning that the salt is slightly soluble. The acidulous part of the name is given in the top line of the table. All the names are in alphabetical order, for facility of reference.

Some of the salts marked as insoluble in water are soluble in aqueous solutions of soluble salts, a few forming soluble double salts. To characterize salts as soluble, slightly soluble, or insoluble, only roughly indicates their relation to water: on the one hand, very few salts are absolutely insoluble in water; on the other, there is a limit to the solubility of every salt.

If only one, two, or perhaps three given acidulous radicals can be in the liquid, test directly for it or them according to the reactions given in the previous pages. If several may be present, pour small portions of the solution, rendered neutral if necessary by ammonia, into five test-tubes, and add respectively sulphuric acid, nitrate or chloride of barium, chloride of calcium, nitrate of silver, and ferric chloride; then consult the Table on page 437, *in order to correctly interpret the effects these reagents may have produced.*

REMARKS ON THE TABLE, page 437.

The first point of value to be noticed in connection with this Table, is one of a negative character; namely, if either of the reagents gives no reaction, it is self-evident that the salts which it decomposes with production of a precipitate must be absent. Then, again, if the action of one of the reagents indicates the absence of certain acidulous radicals, those radicals cannot be amongst those precipitated by tho other reagents; thus, if the action of sulphuric acid points to the absence of sulphides, sulphites, carbonates, cyanides, and acetates, these salts may be struck out of the other lists, and the examination of subsequent precipitates be so far simplified. Or, if the barium precipitate is soluble in hydrochloric acid and the calcium precipitate in acetic acid, neither sulphates nor oxalates can be present. Observing these and other points of difference, which will be seen on careful and thoughtful reflection, and remembering the facts suggested by a knowledge of what basylous radicals are present, one acidulous radical after the other may be struck off as absent or present, leaving only one or two as the objects of special experiment. Among the chief difficulties to be encountered will be the separation from each other of chlorides, bromides, iodides and cyanides, or of tartrates from citrates, and confirmatory tests of the presence of certain compounds. These may all be surmounted on referring back to the reactions of the various radicals, as described under their hydrogen salts, the acids.

In rendering a solution neutral, for the application of the various group-tests, the necessary employment of any large amount of acid or of alkali must be noted, the presence of actual alkalies (that is *hydrates*) or of acids themselves—*free acids*, so-called—respectively, being thereby indicated. Free acids also betray themselves by the *abundant* effervescence which results on the addition of a carbonate.

Sulphuric acid, the first group-reagent, may itself yield, especially when heated with some solid substances, sulphurous acid or hydrosulphuric acid (*see* p. 318); hence the production of the latter acids from a *diluted* solution only is evidence of the presence of a sulphide or sulphite.

In the precipitate produced by chloride of barium, the second group-reagent, the oxalic radical may be specially sought by the test described in the "note" on p. 373.

Chloride of calcium does not precipitate citrates readily or completely in the cold: therefore the mixture should be filtered and the filtrate boiled; calcium citrate then falls. Calcium tartrate is soluble in solution of chloride of ammonium when quite freshly precipitated, but not after it has become crystalline. From their solution in chloride of ammonium, tartrate of calcium is mostly precipitated by ammonia, and citrate on boiling.

The rarer acidulous radicals will very seldom be met with. *Benzoates*, *hippurates* (which give benzoic acid), *hypochlorites*, *hyposulphites*, *nitrites*, and *valerianates* show themselves under the sulphuric treatment. *Ferrocyanides*, *ferricyanides*, *meconates*, *succinates*, *sulphocyanates*, *tannates*, and *gallates*, appear among the salts whose presence is indicated by ferric chloride; *formates*, *hypophosphites*, *malates*, and others by nitrate of silver. *Urates* char when heated, giving an odour resembling that of burnt feathers.

In actual practice the analyst nearly always has some clue to the nature of rarer substances placed in his hands.

If chromium and arsenium have been detected among the basylous radicals, those elements may be present in the form of *chromates*, *arseniates*, and *arsenites*, yielding with chloride of barium yellow chromate of barium and white

TABLE OF THE SOLUBILITY OR INSOLUBILITY OF SALTS IN WATER.

* The asterisk indicates *slight* solubility.	Acetate.	Arseniate.	Arsenite.	Carbonate.	Chloride.	Citrate.	Chromate.	Cyanide.	Hydrate.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Sulphate.	Sulphide.	Sulphite.	Tartrate.
Aluminium	S	I	I	I	S	S*	I	?	I	?	S	I	I	I	S	I	I	S
Ammonium	S	S	S	S	S	S	S	S	S	S	S	S	?	S	S	S	S	S
Antimony	S	I	I	?	S	?	I	?	I	I	?	S*	I	I	I	I	I	I
Barium	S	I	I	I	S	S*	I	S	S	S	S	I	S	I	I	S	I	I
Bismuth	S	I	?	I	S	S*	I	?	I	I	S	I	I	I	S	I	I	I
Cadmium	S	?	?	I	S	S*	?	?	I	S	S	I	I	I	S	I	S	S*
Calcium	S	I	I	I	S	S*	S	S	S*	S	S	I	S*	I	S*	S*	S*	S*
Chromium	S	I	?	I	S	S	I	I	I	S	S	S	I	I	S	I	S	S
Cobalt	S	I	I	I	S	S	?	I	I	S	S	I	I	I	S	I	S*	S
Copper	S	I	I	I	S	S	S	I	I	I	S	I	I	I	S	I	I	S*
Ferric	S	I	I	?	S	S	S	?	I	S	S	S*	I	I	S	I	?	S
Ferrous	S	I	I	I	S	S	?	I	I	S	S	S*	I	I	S	I	S*	S*
Gold	?	I	?	?	S	?	?	I	I	I	?	?	I	?	?	I	?	?
Lead	S	I	I	I	S*	S*	I	I	S*	S*	S	I	I	I	I	I	I	I
Magnesium	S	I	I	I	S	S	S	?	I	S	S	I	I	I	S	?	S	S
Manganese	S	I	?	I	S	I	S	I	I	S	S	I	I	I	S	I	S*	S*
Mercuric	S	I	I	I	S	?	S*	S	I	I	S	I	I	I	S	I	?	I
Mercurous	S*	I	I	I	I	I	I	?	?	I	S	I	I	I	S*	I	?	I
Nickel	S	I	I	I	S	S	I	I	I	S	S	I	I	I	S	I	S*	S*
Platinum	?	I	?	?	S	?	?	?	I	S*	S	?	I	?	S	I	S	?
Potassium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Silver	S*	I	I	I	I	I	I	I	?	I	S	I	I	I	S*	I	I	I
Sodium	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Stannic	S	?	I	?	S	?	I	?	I	S	S	S	I	I	S	I	?	?
Stannous	S	I	I	?	S	?	I	?	I	S	S	I	I	I	S	I	I	S
Strontium	S	I	I	I	S	I	I	S	S	S	S	I	S	I	I	S	I	S*
Zinc	S	I	?	I	S	S*	S*	I	I	S	S	I	I	I	S	I	S*	S*

TABLE TO AID IN THE DETECTION OF CHLORIDES, BROMIDES, IODIDES, CYANIDES, NITRATES, CHLORATES, BORATES, ACETATES, SULPHIDES, SULPHITES, SULPHATES, CARBONATES, OXALATES, TARTRATES, PHOSPHATES, AND CITRATES IN A **NEUTRAL** AQUEOUS SOLUTION.

(For remarks concerning this Table, *see* Pages 434 and 435.)

Sulphuric acid decomposes	Chloride of Barium precipitates	Chloride of Calcium precipitates	Nitrate of Silver precipitates	Ferric Chloride precipitates	Not precipitated
Sulphides. Sulphites. Carbonates, with effervescence — hydrosulphuric and sulphurous acid gases, known by their smell, and carbonic acid gas which has no special odour, being evolved. Cyanides, with production of the odour of hydrocyanic acid. Acetates, with production of the odour of acetic acid when the solution is warmed. (For other salts, *see* p. 435.)	Borates. Sulphites. Sulphates. Carbonates. Oxalates. Tartrates. Phosphates. Citrates. Of these white barium precipitates, the sulphate is the only one insoluble in hydrochloric acid; the tartrate and citrate char when heated on platinum foil; the sulphite and carbonate are decomposed with effervescence by acids.	Borates. Oxalates. Sulphites. Tartrates. Sulphates. Phosphates. Carbonates. Citrates. Of these white calcium precipitates, the sulphate only is sol. in much water; the borate, carbonate, and citrate are sol. in solution of chloride of ammonium: all are sol. in acetic acid except oxalate and some tartrate and sulphate; are all sol. in hydrochloric acid, much sulphate excepted; the dry tartrate and citrate char when heated: the sulphite and carbonate effervesce with acids.	Chlorides, white. Bromides, white. Iodides, yellow. Cyanides, white. Borates, white. Sulphides, black. Sulphites, white. Carbonates, white. Oxalates, white. Tartrates, white. Phosphates, yellow. Citrates, white. Of these silver precipitates, the chloride, bromide, iodide, cyanide, and sulphide are insoluble in dilute nitric acid; the rest soluble.	Borates, yellowish. Sulphides, black. Carbonates, reddish. Oxalates, yellow. Phosphates, yellow-white. Gives red colour with acetates, if neutral. (For other salts, *see* p. 435).	Nitrates. Chlorates. Apply special tests.

Note.—The student should practise the examination of aqueous solutions of salts until able to detect acidulous radicals with facility and precision. For this purpose he may finish the analyses of salts or solutions already examined for common and rarer metals, or have aqueous solutions of salts, or the salts themselves, specially prepared for present use, the metals of the salts being stated. He will then be in a position to effectively study the analysis of salts which may or may not be soluble in water, examining them for both basylous and acidulous radicals (*see* next page).

arseniate and arsenite of barium, and with nitrate of silver red chromate, brown arseniate, and yellow arsenite of silver.

QUESTIONS AND EXERCISES.

In analysing an aqueous solution of salts, for which radicals would you first search, the basylous or the acidulous? and why?—In an aqueous solution there have been found magnesium (Mg) and potassium (K), with the sulphuric radical (SO_4), and iodine (I); state the nature of the salts which were originally dissolved in the water, and mention the principles which guide you to the conclusions.—Give a sketch of the method by which to analyse a neutral or only faintly acid aqueous liquid for the acidulous radicals of salts. In what stage of the process would the following salts be detected? *a.* Carbonates and Sulphates. *b.* Oxalates. *c.* Tartrates and Nitrates. *d.* Acetates and Sulphites. *e.* Bromides and Cyanides. *f.* Borates. *g.* Iodides and Phosphates. *h.* Chlorates, Oxalates, and Acetates. *i.* Chlorides and Iodides. *j.* Sulphites. *k.* Sulphides, Carbonates, and Nitrates. *l.* Citrates and Sulphates.—Nitrate of silver gives no precipitate in an aqueous solution; what acidulous radicals may be present?—Chloride of barium gives no precipitate in a neutral solution, but nitrate of silver a white; what acidulous radicals are indicated?—Ferric chloride produces a deep-red colour in a solution, chloride of calcium yielding no precipitate; what salts may be present? and how may they be distinguished from each other?—Ferric chloride gives a black precipitate in a solution in which sulphuric acid develops no odour; to what is the effect due?

ANALYSIS OF SALTS.

SINGLE OR MIXED, SOLUBLE OR INSOLUBLE.

Thus far all material substances, especially those of pharmaceutical interest, have been regarded as being definite compounds, and as having certain well-defined parts, termed, for convenience, basylous and acidulous respectively: moreover attention has been designedly restricted to those definite compounds which are soluble in water. But there are many substances having no definite or known composition; and of those having definite composition there are many having no definite or ascertained parts. Again, of those having definite composition, and whose constitution admits of the entertainment of theory, there are many insoluble in water.

Chemical substances of whose composition or constitution little or nothing is at present known, are chiefly of animal and vegetable origin, and figure in tables of analyses under the convenient collective title of "extractive matter"; they are not of immediate importance, and may be omitted from consideration.

Of substances which are definite in composition, but whose parts or radicals, if they have any, are unknown or imperfectly known, there are only a few (such as the alkaloids, amylaceous and saccharine matters, the glucosides, and the albumenoid, resinoid, and colorific substances) which have any considerable amount of medical or pharmaceutical interest; these will be noticed subsequently.

Definite compounds most frequently present themselves; and of these by far the larger proportion (namely, the salts soluble in water) have already been fully studied. There remain, however, many salts which are insoluble in water, but which must be brought into a state of solution before they can be effectively examined. The next subject of laboratory work is, therefore, the analysis of substances which may or may not be soluble in water. This will involve no other analytical schemes than those which have been given, will in only one or two cases increase the difficulty of the analysis of a precipitate produced by a group reagent, but will give roundness, completeness, and a practical bearing to the reader's analytical knowledge. Such a procedure will at the same time bring into notice the methods by which substances insoluble in water are manipulated for pharmaceutical purposes, or made available for use as food by plants, or as food and medicine by man and animals generally.

Preliminary Examination of Solid (chiefly mineral) Salts.

Before attempting to dissolve a salt for analysis, its appearance and other physical properties should be noted, and the influence of heat and strong sulphuric acid be ascertained. If the operator knows how to interpret what is thus observed, and to what extent to place confidence in the observations, he may more certainly obtain a high degree of precision in analysis, and will always gain some valuable negative information. But if he has only slight experience of the appearance and general properties of bodies, or has the habit of turning what should be inferences from tentative processes into foregone conclusions, he should omit the preliminary examination altogether, or only follow it out under the guidance of a judicious tutor; for it is impracticable here to do more than hint at the results which may be obtained by such an examination, or to so adapt descriptions as to prevent a student allowing unnecessary weight to preconceived ideas.

Whatever be the course pursued, short memoranda describing results should invariably be entered in the note-book.

1. Examine the physical characters of the salt in various ways, but never, or only rarely and cautiously, by the palate, on account of the danger to be apprehended.

If the salt is white, coloured substances cannot be present; if coloured, the tint may indicate the nature of the substance or of one of its constituents, supposing that the learner is already acquainted with the colours of salts. Closer observation, aided perhaps by a lens, may reveal the occurrence, in a pulverulent mixture, of small crystals or pieces of a single substance; these should be picked out by a needle and examined separately. In a powder or roughly divided mixture of substances, the process of *sifting* (through such sieves as muslin of different degrees of fineness) often mechanically separates substances, and thus greatly facilitates analysis. The body may present an undoubted metallic appearance, in which case only the metals existing under ordinary atmospheric conditions need be sought. Peculiarity in smell reveals the presence of ammonia, hydrocyanic acid, hydrosulphuric acid, etc. Between the fingers a substance is, perhaps, hard, soft, or gritty; consequent inferences follow. Or the matter may be heavy, like the salts of barium or lead; or light, like the carbonates and hydrates of magnesium; or may be one of the pharmaceutically well-known class of "scale" preparations.

2. Place a grain or two of the salt in a small dry test-tube or in a piece of ordinary tubing, closed at one end, and heat it, at first gently, then more strongly, and finally, if necessary, by the blowpipe.

Gases or vapours of characteristic appearance or odour may be evolved; such as iodine, nitrous fumes, sulphurous, hydrocyanic, or ammoniacal gases. Much steam given off by a dry substance indicates either hydrates or salts containing water of crystallization. (A small quantity of interstitial moisture often causes heated crystalline substances to *decrepitate*—from *decrepo*, I crackle—that is, break up with slight explosive violence, owing to the expansive force of the steam suddenly generated.) A sublimate may result, due to salts of ammonium, mercury or arsenium, to oxalic or benzoic acid, or to sulphur free or as a sulphide—a salt wholly volatile containing such substances only. The compound may blacken, pointing to the presence of organic matter—which, in common definite salts, will probably be in the form of acetates, tartrates, and citrates, or as common salts of the alkaloids morphine, quinine, strychnine, or as a starch, sugar, salicin, or in other definite or indefinite forms common in pharmacy, and for which tests will be given in subsequent pages. If no charring occurs, the important fact is established that no organic matter is present—except cyanides, formates, or oxalates, which do not char. The residue may change colour from presence or development of oxide of zinc, oxide of iron, etc., or melt from the presence of a fusible salt and absence of any large proportion of infusible salt, or be unaltered, showing the absence of any large amount of such substances.

3. Place a grain or two of the salt in a test-tube, add a drop or two of strong sulphuric acid, *cautiously* smelling any gas that may be evolved; afterwards slowly heat the mixture, noticing the effect, and stopping the experiment when any sulphuric fumes begin to escape.

Iodine, bromine, and nitrous or chlorinoid fumes will reveal themselves by their colour, indicating the presence of iodides, bromides, iodates, bromates, nitrates, and chlorates. The evolution of a colourless gas fuming on coming into contact with air, and having an irritating odour, points to chlorides, fluorides, or nitrates. Gaseous products having a greenish colour and odour of chlorine indicate chlorates, hypochlorites, or chlorides mixed with other substances. Slight sharp explosions betoken chlorates. Evolution of colourless gas may proceed from cyanides, acetates, sulphides, sulphites, carbonates or oxalates. Charring will be due to citrates, tartrates, or other organic matter. If neither of these effects is produced, most of the bodies are absent or only present in minute quantity. The substances apparently unaffected by the treatment are metallic oxides, borates, sulphates, and phosphates.

4. Exposure of the substance to the blowpipe-flame,—on platinum wire with or without a bead of borax or of microcosmic salt* (phosphate of sodium, ammonium, and hydrogen, $NaNH_4HPO_4$); on platinum foil, or in a porcelain crucible, or on a crucible lid, with or without carbonate of sodium; or on charcoal, alone or in conjunction with carbonate of sodium, cyanide of potassium, or nitrate of cobalt,—will sometimes yield important information, especially to one who has devoted much attention to reactions producible by the blowpipe-flame. The medical or pharmaceutical student, however, will seldom have time to work out this subject to an extent sufficient to make it a trustworthy guide in analysis. (*See* Plattner and Muspratt "On the Use of the Blowpipe," and a chapter in Galloway's "Manual of Qualitative Analysis.")

Methods of Dissolving and Analysing Single or Mixed Solid Substances.

Having submitted the substance to preliminary examination, proceed to dissolve and analyse by the following methods. These operations consist in treating a well-powdered substance consecutively with cold or hot water, hydrochloric acid, nitric acid, nitro-hydrochloric acid, or fusion with alkaline carbonates and solution of the product in water and acid. Resulting liquids are analysed in the manner already described, or by slightly modified processes as detailed in the following paragraphs.

Solution in Water.—Boil about a grain of the salt presented for analysis in about a third of a test-tubeful of water. If it dissolves, prepare a solution of about 20 or 30 grains in half an ounce or more of water, and *proceed with the analysis in the usual way*, testing first for the basylous radical or radicals by the proper group reagents (HCl, H_2S,

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* So called because formerly obtained from the urine of man, who was called the *microcosmos*, or *little world*.

NH_4HS, $(NH_4)_2CO_3$, $(NH_4)_2HPO_4$), pp. 257 or 298, and then for the acidulous radical or radicals, directly or by aid of the prescribed reagents (H_2SO_4, $BaCl_2$, $CaCl_2$, $AgNO_3$, Fe_2Cl_6), p. 437.

If the salt is not *wholly* dissolved by the water, ascertain whether or not any has entered into solution, by filtering, if necessary, and evaporating a drop or two of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with water, for subsequent treatment by acids.

Solution in Hydrochloric Acid.—If the salt is insoluble in water, digest about a grain of it (or of the insoluble portion of a mixed salt) in a few drops of hydrochloric acid, adding water and boiling if necessary. If the salt wholly dissolves, prepare a sufficient quantity of the liquid, noticing whether or not any effervescence (due to the presence of sulphides, sulphites, carbonates, or cyanides) occurs, and proceed with the analysis as before, except that the first step, the addition of hydrochloric acid, may be omitted.

The analysis of this solution will in most respects be simpler than that of an aqueous solution, inasmuch as the majority of salts (all those soluble in water) will be absent. This acid solution will, in short, only contain :—chlorides produced by the action of the hydrochloric acid on sulphides, sulphites, carbonates, cyanides, oxides, and hydrates; and certain borates, oxalates, phosphates, tartrates, and citrates (possibly silicates and fluorides), which are insoluble in water, but soluble in acids without apparent decomposition. The first four—sulphides, sulphites, carbonates, and cyanides —will have revealed themselves by the occurrence of effervescence during solution, and the presence of oxides and hydrates may often be inferred by the absence of compatible acidulous radicals. The borates, oxalates, phosphates, tartrates, and citrates alluded to will be reprecipitated in the general analysis as soon as the acid of the solution is neutralized; that is, will come down in their original state when ammonia and sulphydrate of ammonium are added in the usual course. Of these precipitates, only the oxalate of calcium and the phosphates of calcium and magnesium need occupy attention now; for oxalate and phosphate of barium seldom or never occur, and the borates, tartrates, and citrates met with in medicine or general analysis, are all soluble in water. These phosphates and oxalates, then, will be precipitated in the course of analysis along with iron, their presence not interfering with the detection of any other metal. If, from the unusually light colour of the ferric precipitate, phosphates and oxalates are suspected, it is treated according to the following Table (reference to which should be inserted in the Table for metals, under Fe, p. 257, and in the long Table opposite page 298).

PRECIPITATE OF PHOSPHATES, OXALATES, FERRIC HYDRATE, ETC.

Dissolve in HCl, add citric acid, then NH_4HO, and filter; then follow the Table below.

<table>
<tr><td rowspan="3">Filtrate
Fe.
Add HCl and K_4Fcy.
Blue ppt.</td><td colspan="3">Precipitate
$Ca_3 2PO_4$, CaC_2O_4, $Mg_3 2PO_4$.
Boil in acetic acid, and filter.</td></tr>
<tr><td rowspan="2">Insoluble
CaC_2O_4.*
White.
(CaF_2 *may* occur here.)</td><td colspan="2">Filtrate
$Ca_3 2PO_4$, $Mg_3 2PO_4$.
Add $Am_2C_2O_4$, stir, filter.</td></tr>
<tr><td>Precipitate white, indicating $Ca_3 2PO_4$.</td><td>Filtrate, add AmHO.
White ppt.
$MgNH_4PO_4$.</td></tr>
</table>

In analysing phosphates and oxalates, advantage is also frequently taken of the facts that the phosphoric radical is wholly removed from solution of phosphates in acid by the addition of an alkaline acetate, ferric chloride and subsequent ebullition, as described under "Phosphoric Acid" (p. 390), and that dry oxalates are converted into carbonates by heat, as mentioned under "Oxalic Acid" (p. 373). (*See* also p. 391, 4th Analytical Reaction.)

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* Most oxalates, after being heated, effervesce on the addition of acid; fluorides may be detected by the "etching" test.

Certain arseniates and arsenites, insoluble in water but soluble in hydrochloric acid, may accompany the above phosphates and oxalates if from any cause hydrosulphuric acid gas has not been previously passed through the solution, or passed for an insufficient length of time.

If the substance insoluble in water does not *wholly* dissolve in hydrochloric acid, ascertain if any has entered into solution, by filtering, if necessary, and evaporating a drop of the clear liquid to dryness on platinum foil; the presence or absence of a residue gives the information sought. If anything is dissolved, prepare a sufficient quantity of solution for analysis, and proceed as usual, reserving the insoluble portion of the mixture, after thoroughly exhausting with hydrochloric acid and well washing with water, for the following treatment by nitric acid.

Solution in Nitric Acid.—If the salt is insoluble in water and hydrochloric acid, boil it (or that part of it which is insoluble in those menstrua) in a few drops of nitric acid. If it wholly dissolves, remove excess of acid by evaporation, dilute with water, and proceed with the analysis.

This nitric solution can contain only a few substances; for nearly all salts soluble in nitric acid are also soluble in hydrochloric acid, and therefore will have been removed previously. Some of the metals, however (Ag, Cu, Hg, Pb, Bi), as well as amalgams and alloys, unaffected or scarcely affected by hydrochloric acid, are readily attacked and dissolved by nitric acid. Many of the sulphides, also, insoluble in hydrochloric acid, are dissolved by nitric acid, usually with separation of sulphur. Calomel is converted, by long boiling with nitric acid, into mercuric chloride and nitrate. The nitrates here produced are soluble in water.

This nitric solution, as well as the hydrochloric and aqueous solutions, should be examined separately. Apparently, time would be saved by mixing the three solutions together and making one analysis. But the object of the analyst is to separate every radical from every other; and when this has been partially accomplished by solvents, it would be unwise to again mix and separate a second time. Moreover, solvents often do what the chemical reagents cannot—namely, separate *salts* from each other. This is important, inasmuch as the end to be attained in analysis is not only an enumeration of the radicals present, but a statement of the actual condition in which they are present; the analyst must, if possible, state of what salts a given mixture was originally formed—how the basylous and acidulous radicals were originally distributed. In attempting this, much must be left to theoretical considerations; but a process by which the salts themselves are separated is of trustworthy practical assistance; hence the chief advantage of analysing separately the solutions resulting from the action of water and acids on a solid substance.

Solution in Nitro-Hydrochloric Acid.—If the salt or any part of a mixture of salts is insoluble in water, hydrochloric acid, and nitric acid, digest it in nitro-hydrochloric acid, warming, or even boiling gently, if necessary; evaporate to remove excess of acid, dilute, and proceed as before.

Sulphide of mercury and substances only slowly attacked by hydrochloric or nitric acid, as, for example, calomel and ignited ferric oxide, are sufficiently altered by the free chlorine of aqua regia to become soluble.

Analysis of Insoluble Substances.

If the substance is insoluble in water and acids, it is one or more of the following substances:—Sand and certain silicates, such as pipeclay and other clays; fluor spar; cryolite ($3NaF, AlF_3$); sulphates of barium, strontium, and possibly calcium; tinstone; antimonic oxide; glass; felspar (double silicate of aluminium and other metals); chloride, bromide, or iodide of silver; sulphate of lead. It may also be or contain carbon or carbonaceous matter, in which case it is black and combustible, burning entirely or partially away when heated in the air—or be or contain sulphur, in which case sulphurous gas is evolved, detected by its odour, when the substance is heated in air. A drop of solution of sulphydrate of ammonium, added to a little of the powder, will at once indicate the presence or absence of salts of such metals as lead and silver. For the other substances, proceed according to the following (Bloxam's) method :—

Four or five grains of the dry substance are intimately mixed with twice the quantity of dried carbonate of sodium, and this mixture well rubbed in a mortar with five times its weight of *deflagrating flux* (1 of finely powdered charcoal to 6 of nitre). The resulting powder is placed in a thin porcelain dish, or crucible, or clean iron tray, and a lighted match applied to the centre of the heap. Deflagration ensues, and decomposition of the various substances occurs, the acidulous radicals going to the alkali metals to form salts soluble in water, the basylous radicals being simultaneously converted into carbonates or oxides. The mass is boiled in water for a few minutes, the mixture filtered, and the residue well washed. The filtrate may then be examined for acidulous radicals and aluminium, and the residue be dissolved in diluted hydrochloric acid and analysed by the ordinary method.

The only substance which resists this treatment is chrome iron-ore.

To detect alkali in felspar, glass, or cryolite, Bloxam recommends deflagration of the powdered mineral with one part of sulphur and six of nitrate of barium. The mass is boiled in water, the mixture filtered, hydrate and carbonate of ammonium added to remove barium, the mixture again filtered, and the filtrate evaporated and examined for alkalies by the usual process.

Hydrates and Oxides.

If no acidulous radical can be detected in a substance under analytical examination, or if the amount found is obviously insufficient to saturate the quantity of basylous radical present, the occurrence of oxides or hydrates, or both, may be suspected. Confirmation of their presence will be found in the general rather than in any special behaviour of the substances. Some hydrates yield water when heated—in a dry test-tube held nearly horizontally in a flame, so that moisture may condense on the cool part of the tube. Some oxides yield oxygen—detected by heating in a test-tube, and inserting the incandescent end of a strip of wood. Soluble hydrates cause abundant evolution of ammonia gas when heated with solution of chloride of ammonium. Soluble hydrates also give characteristic precipitates with the various metallic solutions. Hydrates and oxides insoluble in water, not only neutralize much nitric acid, or acetic acid, but are thereby converted into salts soluble in water. Most oxides and hydrates have a characteristic appearance. In short, some one or more properties of an oxide or a hydrate will generally betray its presence to the student who not only has knowledge respecting chemical substances, but has cultivated the faculties of observation and perception.

Fractional Operations.

Not only is the common process of *sifting* (p. 440) through sieves of varying degrees of fineness a useful fractional operation or separatory adjunct in analytical as in other work, but also fractional *elutriation* (p. 149), fractional *solution* of a mixed mass by *lixiviation* (p. 94) of the substance with successive small quantities of solvents, and fractional *precipitation* with filtration after each addition of successive small quantities of a precipitant. Fractitional *distillation* (*vide* Index) is often very useful, fractional *sublimation* (p. 100) and fractional *crystallization* (p. 81) occasionally, fractional *fusion* less often.

QUESTIONS AND EXERCISES.

Describe the preliminary treatment to which a salt may be subjected prior to systematic analysis.—Mention substances which might be recognised by smell.—Which classes of salts are heavy, and which light?—Name some bodies detectable by their colour.—What inference may be drawn from the appearance of steam when dry substances are heated?—Why do certain crystals decrepitate?—If a powder sublimes on being heated, to what classes of compounds may it belong?—When heat causes charring, what conclusion is drawn?—No change occurring by heat, which substances cannot be present?—Give examples of salts which are identified by their reaction with strong sulphuric acid, and by their comportment in the blowpipe-flame, with or without borax or microcosmic salt.—What are the solvents usually employed in endeavouring to obtain a substance in a state of solution? and what is the order of their application?—Name a few salts which may be present in an aqueous solution.—Mention some common compounds insoluble in water, but soluble in hydrochloric acid.—What substances are only attacked by nitric acid or nitro-hydrochloric acid?—At what stage of analysis do arsenites and arseniates show themselves?—Sketch out a method for the complete analysis of a liquid suspected to be an aqueous solution of neutral salts.—How can earthy phosphates and oxalates with ferric oxide be separated from each other?—How would you proceed to analyse an alloy?—By what process may substances insoluble in water or acids be analysed?—How would you qualitatively analyse glass?

RECAPITULATORY AND OTHER NOTES ON THE CONSTITUTION OF THE DEFINITE CHEMICAL COMPOUNDS COMMONLY TERMED SALTS.

The molecules of a salt (p. 32) contain *radicals* (p. 68) which may be either elementary or compound (p. 69).

Each radical has a definite exchangeable value (p. 135).

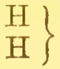
The definite exchangeable values of radicals differ in different series of radicals (pp. 135 to 137).

In one and the same molecule of a salt, two or more different atoms of the same element may possess the two distinct functions of being (*a*) a single definite distinct radical, and (*b*) one member of a group of atoms which together form a single definite distinct radical (pp. 136 and 305).

The relation to each other, either of the elementary or the compound radicals in *organic* substances or salts, is apparently far more complex than the relation to each other of the elementary or compound radicals in inorganic or mineral salts—as will be apparent when the section on organic chemistry has been studied.

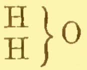
The properties of salts are regarded as depending on (*a*) the nature, (*b*) the number, and (*c*) the position in relation to each other, of the elementary and compound radicals in a molecule—as will be apparent when the subject of isomerism has been studied.

Dumas, afterwards Laurent, and then Gerhardt, attempted the classification of salts under such *types* as the following:—



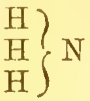
$$\left.\begin{matrix} H \\ H \end{matrix}\right\}$$

The hydrogen type.



$$\left.\begin{matrix} H \\ H \end{matrix}\right\}O$$

The water type.



$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N$$

The ammonia type.

Other chemists have extended the number of such types of salts. Further, by writing the typical formulæ in the above and other manners, a mode of indicating the facts assumed to be dependent on the position of the atoms in a molecule has been sought to be obtained. Finally, the natural development of this train of thought and of practice has produced the *graphic formulæ* of Kékulé, Frankland, and others, and has given rise to the doctrine of *valency*.

Caution.—The conjectural or theoretic character of our ideas respecting masses of matter being formed of molecules, and molecules of atoms, and that molecules contain radicals consisting of one or more atoms, must never be lost sight of, highly valuable and practically useful though the hypotheses be (see pages 30, 49 to 56, 155, 306, 333, 350, 461).

Berthollet's Laws.—"When we cause two salts to react by means of a solvent, if, in the course of double decomposition, a new salt can be produced less soluble than those which we have mixed, this salt will be produced." "When we apply dry heat to two salts, if, by double decomposition, a new salt can be produced more volatile than the salts previously mixed, this salt will be produced."

Malaguti's Law.—When solutions of two different salts are mixed and metathesis occurs, and four salts result; the proportions of the salts to each other are dependent on the strength or intensity of force with which the respective basylous and acidulous radicals are united.

The state of equilibrium just mentioned may be permanent or temporary. The latter condition obtains when one of the salts which may possibly be produced is insoluble, for as soon as precipitation occurs the equilibrium is upset, and is re-established only to be upset again, and so on until from the four salts there result one in solution and one out of solution. This would seem to be the way in which the laws termed "Berthollet's" work.

The Periodic Law.—Observations by Newlands, elaborated by Mendelejeff and Lothar Meyer, point to a law thus expressed by the latter chemist:—"If the elements are arranged in order of increasing atomic weights [by which the student will understand those actual combining weights conveniently termed atomic weights], the properties of these elements vary from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series." For example:—

Li Be B C N O F Na Mg Al Si P S Cl K Ca, etc.

The periodicity of properties here alluded to occurs at about every eighth member of the series, irresistibly suggesting the periodicity of the musical scale. Thus sodium becomes the octave to lithium, silicon to carbon, phosphorus to nitrogen, sulphur to oxygen, chlorine to fluorine, potassium to sodium, calcium to magnesium, etc. Each chemical note (element) is distinct from the other, yet there is this curious harmony between any one and the eighth on either side. There are gaps in some of the series suggesting elements yet to be discovered, and irregularities suggesting the desirability of reconsidering some of the present weights; and other difficulties occur. Clearly the properties of the elements are in some way dependent on their "atomic" weights; the properties would indeed seem to be mere functions of these weights; the properties would seem to be determined by the weights; at all events there is some such relationship between the elements—all of which facts and considerations, by the way, irresistibly suggest the actual existence of *atoms* having fixed weight, and, *pro tanto*, very strongly support Dalton's atomic theory. Evidently there is less of fundamental difference between the so-called elements than we assume when we regard them as *distinct elements*. They would seem to be not so distinct as we commonly imagine. Whence the observed relationship of lithium, sodium, and potassium; of nitrogen, phosphorus, arsenium and antimony (pp. 186, 392); of oxygen, sulphur, selenium and tellurium (p. 354); of carbon, silicon and perhaps boron (p. 420); of chlorine, bromine, iodine (p. 323) and fluorine (p. 405)? Are the so-called elements one and the same matter differing only in the weight of their ultimate particles? Is the difference only, say, rate of vibration? They have not *yet* been transmuted. The subject is not developed sufficiently to warrant farther consideration in this manual, for ordinary medical and pharmaceutical students. Other students will find it fully considered in more advanced works. Papers and general statements will also be found in most journals of pharmacy (see *Pharmaceutical Journal*, 3rd ser., vol. xviii. p, 882).

ADVICE TO STUDENTS

Respecting the Method of Studying the following pages on Organic Chemistry.

Both medical and pharmaceutical students of organic chemistry may be divided into two classes, namely : *junior students*, or those who, in the first instance at all events, desire to obtain only a general acquaintance with the subject, and *senior students*, or those who, having some general information, desire more complete and thorough knowledge of this branch of the science. To the members of each of these classes who use this Manual, some advice concerning the kind and extent of work they may hope to accomplish in this department of the science will perhaps be acceptable.

Junior Students.—The whole of the following section on organic chemistry should be read through carefully once or twice, with the object, not so much of remembering all that is stated, as of acquiring (*a*) a general view of the scope of the subject, (*b*) a clear notion of the modes of classifying organic substances, and (*c*) an intelligent perception of their broad relationships to one another. (*d*) Special attention should be given to the methods of preparing and testing the particular substances officially recognised in the British Pharmacopœia, the student of practical chemistry preparing actual specimens of most of these substances, as well as going through tests for them and testing for impurities in them. He should make small quantities of chloroform, iodoform, spirit of nitrous ether, acetic ether, and a volatile oil ; should extract gum from a gum-resin, purify some benzene, test aloin, and examine methylated spirit for its methylic constituent; prepare some spirit of wine by fermentation, concentrating the product until it will burn ; make ether ; convert amylic alcohol into valerianic acid ; test carbolic acid and glycerine ; manufacture a little soap ; extract mannite from manna ; go through the analytical reactions of cane and grape sugar ; obtain starch from wheat-flour, maize-flour, and a potato, and examine each product with the microscope ; make dextrin, pyroxylin, and collodion ; prepare and test aldehyde, and try the action of lime on chloral hydrate ; prepare and test acetic, oxalic, and citric acids ; emulsify sweet and bitter almonds : prepare elaterin and test jalap-resin and salicin ; extract morphine or quinine, or both, and perform the tests for the chief alkaloids of opium, cinchona, and nux vomica; test albumen and pepsin. Having gone through these operations, he should again read through the whole section.

Senior Students, having done all that junior students are, in the previous paragraph, advised to do, should thoughtfully study every page, reading what one other author, at least, has to say on each subject. More especially they should actually prepare, or test, or otherwise *experiment* with, one or more typical members of most of the series, or sub-series, of organic bodies. For example, they should prepare the *hydrocarbon* methane (from acetate of sodium), convert it into a *haloid derivative* (by one of the given methods), transform this into the *alcohol* (by the agency of oxide of silver and water), and this again into the *acid* (by oxidation). The preparation of acetylene, and ethylene, and some of their derivatives, should be tried; the differences between turpentine and petroleum spirit be experimentally proved; nitrobenzene be made, this be converted into aniline, and this again into "mauve"; aloin should be prepared; methylic alcohol be extracted from crude wood spirit and absolute alcohol be obtained from spirit of wine; alcohol and acetic acid be regenerated from the acetic ether previously prepared (by ebullition with a strong aqueous solution of potash); iodide or bromide of ethyl and perhaps zinc-ethyl be made; glycol be prepared and then be oxidized; glycerine be examined; starch be converted into dextrin and into sugar; malt extract be examined for diastase; trinitrocellulin be made; acetic aldehyde be fully examined and aldehyde-ammonia be prepared; lactic acid be made; benzoic and salicylic acids and aldehydes be obtained; natural urea be extracted and artificial urea be made; the glucosides be examined; and one or two artificial alkaloids be prepared; etc. Melting-points and boiling-points of pure substances should be taken; and fractional distillation should be applied either to acetic acid with a view to separate glacial acid on the one hand from water or weak aqueous acid on the other, to mixed alcohol and water with the object of attempting their re-separation as far as possible, or to some such mixture. Especially must the operations of quantitative analysis of organic compounds, in due time, be fully and thoroughly performed.

Other Students.—Students who have no occasion to apportion their periods of study in the manner contemplated in the previous paragraphs are recommended to go through the succeeding sections as they have gone through the foregoing, namely, page by page.

Note.—Students will find that in working at organic chemistry so-called, they are not departing from the method of study hitherto pursued. Hitherto they have concentrated attention on the chief elements, one at a time; they are now about to investigate the compounds of another of those elements, that is all. But it is an element having a greater range of combining powers than any yet examined. Organic chemistry is the chemistry of the element *carbon.*

ORGANIC CHEMISTRY;*

OR

THE CHEMISTRY OF CARBON COMPOUNDS.

INTRODUCTION.

Except alcohol and a few acids, the large number of compounds which have hitherto engaged notice in this Manual have been of mineral origin. But the two other kingdoms of Nature, the animal and vegetable, furnish still larger numbers of definite substances. These latter compounds, indeed, when discovered, were producible *only* by organized living structures, hence were termed, more than 200 years ago, *organic* (from *ὄργανον*, *organon*, an organ), and their study was termed *organic chemistry.* A very large number of organic compounds can now, however, be obtained artificially —without the aid of a living organism; hence the particular distinction formerly drawn between organic and inorganic compounds, "organic" and "inorganic" chemistry, no longer fully obtains. Another definition, or additional definition of organic chemistry, or the chemistry of animate nature, the laws of which do not differ from those of inanimate nature, is now generally adopted, namely, *the chemistry of carbon compounds.* No doubt two or three kinds of compounds of carbon—carbonic acid gas and carbonates, for example— are met with in the mineral kingdom, and are therefore inorganic compounds; but they are met with in the organic kingdoms too, and therefore are organic compounds also.

Practically, all carbon compounds are organic compounds, and all of the so-called organic compounds are carbon compounds, hence the old term, *organic chemistry*, no longer being etymologically and fully applicable, that of *the chemistry of the carbon compounds* seems natural as well as useful.

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* Read the two previous pages of *Advice to Students.*

Moreover, the carbon atoms possess in an altogether exceptional degree a property either not possessed or only to a much slighter extent possessed by those of other elements, namely, the property of combining with one another, and forming a sort of chain, to every link of which atoms of other elements can be attached, the result being obviously molecules of almost infinite variety and complexity; a fact which alone suffices to secure for carbon special and separate consideration by chemists. In short, the chemistry of the carbon compounds includes what was formerly as well as what is now known as organic chemistry ; or, in other words, the chemistry of organized or animate nature is included in the chemistry of the carbon compounds. Of course, so old and historically interesting a term as *organic chemistry* will continue to be used ; and there is no objection to such use, provided students remember that when the term is used as the equivalent of *the chemistry of the carbon compounds*, it is only conventionally and not etymologically accurate. Moreover, the chemistry of a carbon compound includes the chemistry of every element in that compound and the chemistry of the compound as a whole, facts which obtain even more prominence if the chemistry be spoken of by a general word such as *organic*, rather than by the specific word *carbon*. Indeed, those organic compounds which contain nitrogen seem to be conditioned as much by their *nitrogen* as their carbon. So that, the word *organic*, having now in chemistry lost its original specific signification, and having acquired the general signification described, it becomes, by its associations, perhaps the best word that can be chosen as the title of the great division of chemistry now under consideration.

COMPOSITION OF ORGANIC COMPOUNDS.

(*a*) *Qualitative Composition.*—The presence of carbon in a compound is at once shown if the compound blackens when a little is heated on a knife or platinum foil in a flame. If the substance is heated in a dry, narrow test-tube, and much moisture is condensed on the upper cool part of the tube, the presence of hydrogen and oxygen are reasonably inferred. Nitrogen may be detected by the odour of ammonia emitted on strongly heating the substance with a dry mixture of soda and lime; or it may be sought by carefully but strongly heating in a test-tube a small portion of the substance with a very small piece of sodium, and, after all action ceases, digesting the residue in water, filtering, and adding to the filtrate a ferrous salt, a ferric salt, and hydrochloric acid; a precipitate of Prussian blue indicates nitrogen. Chlorine, bromine, iodine, sulphur, and phosphorus may be detected by heating the substance with nitric acid and nitrate of silver in a very carefully and strongly sealed tube (in a fume-chamber, with such precautions that if the tube burst no harm to the operator shall ensue), and testing the product for chlorides, bromides, iodides, sulphates, and phosphates, by methods already described.

(*b*) *Quantitative Composition.*—The qualitative composition of an organic substance being ascertained, the quantities of each element are then determined by methods which the student will practise when he is sufficiently advanced to work at the sections on quantitative analysis. The principles of the methods, are, however, simple, and may at once be described. For the quantitative estimation of *carbon* and *hydrogen*, a carefully weighed portion of the substance is completely burned; the products, which are, of course, carbonic acid gas and water, are collected and accurately weighed. Of every 44 parts of the carbonic acid gas ($CO_2=44$), 12 will be carbon, and of every 18 parts of the water ($H_2O=18$), 2 will be hydrogen; in other words, three-elevenths of the weight of carbonic acid gas obtained will be the carbon of the original substance, while one-ninth of the water obtained will be the hydrogen of the original substance. If *nitrogen* be present, another weighed portion of the substance is so burned as to yield all its nitrogen as gas which is carefully collected and measured, or it is heated with a mixture of soda and lime, when the nitrogen takes up hydrogen and becomes ammonia, which is collected and accurately estimated; of every 17 parts of ammonia ($NH_3=17$), 14 will be nitrogen. The amounts of *chlorine*, *sulphur*, etc., elements not often present, are obtained by subjecting carefully weighed portions of the original substance to the nitric treatment already alluded to, collecting and weighing the products, and calculating what proportions of the products are chlorine, sulphur, etc. The amount of *oxygen* is ascertained by difference, that is to say, the difference between the sum of the weights of carbon, hydrogon, nitrogon, otc., and the original weight of substance will be the weight of the oxygen in that original weight of substanco.

For example, a fluid having well-marked definite properties, and known to contain only carbon, hydrogen, and oxygen, is so burned that 0·3 of a gramme* of it yields 0·5738 of a gramme of carbonic acid gas, and 0·3521 of water. As three-elevenths of the carbonic acid gas is carbon, and one-ninth of the water is hydrogen, it follows that the 0·3 of substance contains 0·1565 of carbon and 0·0391 of hydrogen; and the difference between these two figures and 0·3 being 0·1044, it follows that 0·1044 is the amount of oxygen in the 0·3 of original substance. For, $0{\cdot}5738 \times 3 \div 11 = 0{\cdot}1565$; and $0{\cdot}3521 \div 9 = 0{\cdot}0391$; $0{\cdot}3 - (0{\cdot}1565 + 0{\cdot}0391) = 0{\cdot}1044$.

(*c*) *Centesimal Composition.*—It is usual to make at least two such analyses of any organic compound; and as different weights of the original substance will almost necessarily be subjected to combustion (for it is easier to counterpoise by weights a selected quantity than it is to counterpoise with the substance any selected weights), the results of the combustions can best be compared by converting the numbers first obtained into percentages; that is to say, by assuming in, for instance, the present case, that not 0·3 parts of substance were operated on, but 100 parts. This is one of the simplest of arithmetical operations. If 0·3 of substance yields 0·1565 of carbon, 100 of substance will yield 52·17 of carbon. If 0·3 of substance yields 0·0391 of hydrogen, 100 of substance will yield 13·03 of hydrogen. And if 0·3 of substance yields 0·1044 of oxygen, 100 of substance will yield 34·80 of oxygen.

(*d*) *Chemically Empirical Composition.*—But the chemist further desires to know, not so much what percentages or ordinary unit-weights of elements are contained in the compound, but what relative number of chemical unit-weights or atomic weights are present; how many parts of carbon each weighing twelve, how many parts of hydrogen each weighing one, how many parts of oxygen each weighing sixteen, how many parts of nitrogen each weighing fourteen, etc. This too is one of the simplest of arithmetical operations. Divide the percentage of carbon by 12, of hydrogen by 1, of oxygen by 16, of nitrogen by 14, etc. Thus, in the present case:—$52{\cdot}17 \div 12 = 4{\cdot}347$ atomic weights of carbon;

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* If the reader is not already familiar with the metric system of weights and measures, he is referred to the section on that subject in the latter part of the Manual.—(*Vide* Index, "Metric System.")

13·03 ÷ 1 = 13·03 atomic weights of hydrogen; and 34·80 ÷ 16 = 2·171 atomic weights of oxygen. Reducing these three fractional numbers of atomic weights to the lowest whole numbers (by assuming that the lowest of the three will represent 1 atomic weight—that is, by dividing the two higher of the three by the lowest), we find that the compound is composed of 2 atomic weights of carbon, 6 of hydrogen, and 1 of oxygen, thus:—4·347 ÷ 2·171 = 2 of carbon; 13·03 ÷ 2·171 = 6 of hydrogen; 2·171 ÷ 2·171 = 1 of oxygen. The result is that of proportions of carbon each weighing 12, the substance contains 2; of proportions of hydrogen each weighing 1, the compound contains 6; and of proportions of oxygen each weighing 16, the compound contains 1. Finally, instead of the words "proportion of carbon weighing 12," the simple capital letter C may be used, which, as the reader now well knows, is not only the shorthand or symbol for the word carbon, but stands for 12 parts of carbon. Similarly H may stand for 1 part of hydrogen, and O for 16 parts of oxygen; whence we arrive at C_2H_6O as the simplest chemically empirical expression, or *empirical formula*, of the substance under consideration.

(*e*) *Chemically Rational Composition.*—From the *empirical formula* of a substance we pass to a *two-volume formula;* that is to say, in accordance with the practice of chemists, the formula must, if possible, represent two volumes of the substance when in the state of vapour (see pp. 54 and 58). Two parts of hydrogen gas, or seventeen of ammonia gas, or eighteen similar parts of water vapour, or forty-four of carbonic acid gas, or thirty-six and a half parts of hydrochloric acid gas, etc., occupy, if all are at the same temperature and under the same pressure, the same volume; whence we derive the formulæ H_2, NH_3, H_2O, HCl, and CO_2 as formulæ comparable with each other. If now the vessel which held these quantities of the respective substances be filled with the vapour of the substance supposed to be under examination at the same temperature and pressure, and the vessel and contents be weighed, the contents will be found to weigh 46 similar parts. C_2H_6O will be found, on adding up the atomic weights, to represent 46 parts by weight. Therefore C_2H_6O is the two-volume formula as well as the empirical formula, and thus the first step has been taken from the formula chiefly obtained by chemical art, *an empirical formula*, towards one largely obtained by, and that satisfies, the reason—*a rational formula* or *structural* or *constitutional formula.* Had the weight been found to be 92, the two-volume formula would have been $C_4H_{12}O_2$. The actual method of taking these weights of equal volumes of gases and vapours (specific gravity and vapour-density) will be described in the paragraphs on quantitative analysis.

(*f*) *Molecular Composition.*—Equal volumes of gases and vapours being similarly affected by temperature and pressure must be similarly constituted (Avogadro and Ampère's conclusion, pages 52 and 53). Whatever the number of molecules in such equal volumes may be, it must be the same in each. Therefore the weights of equal bulks of gases and vapours under like conditions represent the relative weights of the respective molecules. Hence 2, 17, 18, 44, and 36·5 respectively represent the weight of one molecule of each of the substances hydrogen, ammonia gas, water vapour, carbonic acid gas, and hydrochloric acid gas; and 46 represents the molecular weight of the substance under consideration. C_2H_6O therefore represents the composition of a molecule of the substance. C_2H_6O is the *molecular formula* of the substance. (The substance is common alcohol.)

Acetic acid will serve as another simple illustration. Analysis and arithmetic yield the formula CH_2O. But metals only displace one-fourth of the hydrogen in any given weight of acetic acid. That fact cannot be shown by the formula CH_2O, but it can by the doubled formula $C_2H_4O_2$. This *chemical* evidence that the latter formula is, so far, correct, is supported by the *physical* evidence of vapour-density as interpreted in the previous paragraph. *See* also "Vapour-density," and "Raoult's Experiments" in Index.

Check on Composition.—If the formula found is, even so far, the true formula of the substance, the centesimal composition found by experiment ought to be practically the same—the same within the limits of experimental error—as the centesimal composition obtained by calculation from the formula, thus:—

	Calculated	Found
$C_2 = 24$	52·174	52·170
$H_6 = 6$	13·043	13·030
$O = 16$	34·783	34·800
46	100·000	100·000

From *composition* we now pass to *constitution*. What we know of the composition of a substance is reflected in its *empirical formula*. A step in advance is recorded in the *molecular formula*. What is afterwards learnt about *constitution* is exhibited in the *structural formula*. If the letters in a formula, for instance C_2H_6O, be regarded only as representing fixed weights, the formula expresses only facts; but we also regard the letters as representing *atoms* (Dalton's theory); and the whole formula as representing a *molecule* (Avogadro's theory); while in attempting structural formulæ we further depend on the idea of the valency of atoms. To this subject of *structure* or *constitution* we now pass.

CONSTITUTION OF ORGANIC COMPOUNDS.

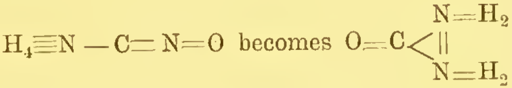
In the molecule of an organic compound, how are the atoms arranged? This is perhaps the greatest problem the chemist has to solve. Like the toy-puzzles of our youth, these chemical puzzles have to be attacked analytically and synthetically. How to separate into its constituent bars of wood that apparently solid cube given to us by a friend in old days, was not an uncongenial task; but, once accomplished, how to put these bars together again was a still more fascinating if more difficult labour. How to separate the groups of atoms or radicals in molecules of chemical substances, or at least how to find out the positions of those groups in a molecule, is a most difficult yet fascinating task for the skilled enthusiast in chemistry; and how to so marshal those groups (drawn perhaps from several different sources, and visible and tangible only in a state of combination and in mass) that he shall produce by art the compound originally only furnished by Nature, is still more difficult but also more fascinating. More fascinating firstly, because it will furnish proof that his synthetical work was sound; secondly, because by artificially and perhaps cheaply producing a rare colour, a rare perfume, a rare flavour, or a previously costly medicine, he may become a benefactor to his fellow-man; and thirdly, because he may gain the honour of unveiling for all time one more of the truths of Nature.

In practically attacking the problem of the constitution of a compound, the chemist proceeds to note whether the substance is acid, alkaline, or neutral; to act on it with a base of known constitution if it is an acid, or with an acid of known constitution if it is a base, and to analyse the produced salts; to oxidize it; to deoxidize it; to chlorinize it; to remove or add hydroxyl (HO), carbonyl (CO), etc.; to substitute hydrogen by a compound radical, and *vice versâ*; to heat it; to electrolyse it; and, generally, to perform many such operations, in the hope that the lines of chemical cleavage in the molecule will be detected, the essential groupings of atoms in the molecule be discovered, and even the positions of atoms or groups of atoms in relation to each other be reasonably inferred. Briefly, similarity in properties implies similarity in constitution or structure. *Per contra*, similarity in structure being reasonably implied, reference to properties shows whether or not the reason is on the right track towards truth in the matter of constitution or structure, the advance towards error being prevented and towards truth being maintained whatever be the result of the reference, new truths not infrequently being unveiled. Thus, by the way, in chemistry, do fact and theory ever discharge their obligations to each other.

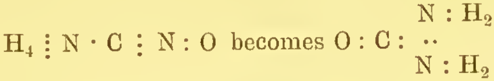
For example, urea, which was the first organic body produced artificially, was obtained by Wöhler in 1828 on heating solution of cyanate of ammonium; H_4NCNO became $OC(NH_2)_2$, the mere change in the position of the constituent atoms, that is, in the *structure* of the molecules (indicated roughly, but to the best of our judgment, by the change in the relative position of the letters in the two formulæ just given) accounting for the differences in the properties of the two substances—just as the differences in the relative position of a given number of stone blocks which at first were put together to form a bridge, but afterwards were put together to form a house, that is, the differences in the *structure* of the edifices, account for the differences in their properties.

Notation of Organic Compounds.

In order that we may convey to one another our conclusions respecting the constitution of organic compounds, notation has to be carried somewhat farther in organic than has already been shown to be necessary in inorganic chemistry (see pages 36 and 42). The relative position of atoms and groups of atoms in a molecule may be indicated by placing the symbolic letters above or beneath one another as well as on one line, and the quantivalence of atoms, as well as the directions in which we conclude they are joined in the molecule, may be indicated by lines ($-\ =$ or $\equiv$) or dots (·:⁝) either completely or only partially employed throughout the formula; each dot, and, especially, each line or "bond," or "link" representing such union between two neighbouring atoms or radicals as would be represented by the extended arms of two persons shaking hands. For instance the statement just made that cyanate of ammonium (H_4NCNO) becomes urea [empirically CH_4N_2O, or rationally $OC(NH_2)_2$] might be represented by either of the following forms of equation:—



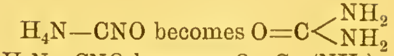
$$H_4{\equiv\!\!\equiv}N-C\equiv N=O \text{ becomes } O=C{<}\begin{array}{l}N=H_2\\ \ \|\\ N=H_2\end{array}$$



$$H_4 \vdots\!\vdots\, N\cdot C \vdots\, N:O \text{ becomes } O:C:\begin{array}{l}N:H_2\\ \ \ \cdot\cdot\\ N:H_2\end{array}$$

Here, bars, in the first equation, and dots in the second, show not only the quantivalence, but especially the distribution of the chemical affinity expressed by the quantivalence of each atom. Thus the first four bars or dots not only indicate the univalence of each of the four hydrogen atoms on the one hand, and four-fifths of the quantivalence of the first nitrogen atom on the other hand, the next bar or dot showing the remaining fifth, but the five bars or dots also indicate that of the total affinity of the nitrogen atom, four-fifths are engaged with a corresponding amount of attraction offered by four univalent hydrogen atoms, while the other fifth is engaged with one-fourth of the total attraction of the adjacent carbon atom. And so on with the quadrivalence of the carbon atom, the quinquivalence of the second nitrogen atom, and the bivalence of the oxygen atom.

But it is unnecessary, indeed undesirable, thus to indicate the quantivalence of *each* atom in a molecule, the closeness of union of groups of atoms (radicals) within a molecule being best indicated by putting the symbolic letters in a formula as close together as written characters or printer's types will allow; moreover an atom, such as that of nitrogen, may often pass from one degree of activity to another during a reaction. The following, therefore, are better arrangements:—

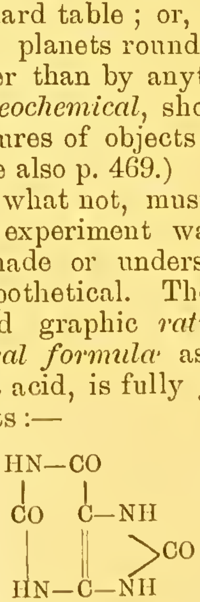


$H_4N{-}CNO$ becomes $O{=}C{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$

$H_4N \cdot CNO$ becomes $O : C : (NH_2)_2$.

Indeed, after a time the chemical student will find that his own imagination will often best supply that which is intended to be indicated by the lines or dots in the formulæ of organic compounds, actual lines or dots only being employed where their use tends to promote clearness in a formula. For printed lines look like bars, and these, and even dots, are liable to suggest separation, whereas in a chemical formula they should suggest the union of the atoms and radicals in the molecule of which the formula is the crude picture. While suggesting links and bonds, however, and the affinity (quantivalence or valency) of the atoms, they must be regarded as indicating lines of force rather than anything more substantial. Again, symbols and formulæ, written or printed, are necessarily exhibited on surfaces, whereas the conception of a molecule should be that of a sphere—that of grapes on a bunch, or apples on a tree, rather than balls on a billiard table; or, still better, that of moons round a planet and planets round a sun, all kept in their places by force rather than by anything material; our conceptions should be *stereochemical*, should be stereoscopic pictures rather than pictures of objects on a plane surface without perspective. (See also p. 469.)

Finally, bars, dots, or what not, must only be placed in a formula where actual experiment warrants, unless the statement is distinctly made or understood that the suggested formula is only hypothetical. The use of such apparently highly complicated graphic *rational formulæ* or *constitutional* or *structural formulæ* as, for example, the following formula for uric acid, is fully justified by a series of well-defined experiments:—



Here, not only is the univalence of each of the hydrogen atoms, the bivalence of oxygen atoms, the trivalent character of each of the nitrogen atoms, and the quadrivalent nature of each carbon atom shown, either directly by bars attached to the symbols or suggestively by the position of a symbol of recognised quantivalence next to another symbol of recognised quantivalence, but the positions which experiment warrants us in believing that the radicals occupy within the molecule are indicated in the formula by the position of the symbols for those radicals (HN, imidogen; CO, carbonyl) near central atoms of carbon.

To the student the great advantage of extended formulæ, whether ordinary or graphic, consists in the relationships which they clearly exhibit between compounds which otherwise are not readily shown to be related to one another. The *constitution* or *structure*, so far as can at present be inferred, of chemical compounds of interest to the medical or pharmaceutical student, will be found to be given, when desirable, in this Manual. Students who desire to pursue the subject more fully must seek other guides.

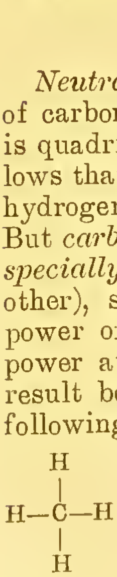
The structural formulæ characteristic of modern chemistry may be regarded as pictures of our idea of architecture in Nature's molecules. The first sketches are seen in such formulæ as $HC_2H_3O_2$. Among the earlier mid-century artists were Gerhardt, Williamson, Frankland, and especially from 1858 onwards, Kekulé.

Caution.—Our conception of the structure or constitution of masses or *moles* of matter, or of particles or *molecules*, or of the *atoms* of which we conceive molecules are composed, or of the *valency* of those atoms, are nothing more than conceptions. All varieties of *chemical formulæ* are but concrete reflections or pictures of those conceptions. Why do we make those conceptions, and why do we thus picture those conceptions? We make them because, firstly, the enormous number of facts that chemistry unfolds creates, in the healthy human mind, a demand for classification; and, secondly, because the healthy human mind instinctively demands the reason *why* facts are as they are. And why do we adopt the existing chemical formulæ as concrete reflections of our abstract ideas? Because, firstly, intercommunication between minds can only be accomplished satisfactorily either by human utterances or by those written or printed equivalents, or signs, or symbols, of speech termed letters, etc. (singly or combined to form words, etc.); and, secondly, because, as regards any one mind, the desire to avoid utter mental confusion demands the adoption of some method of concretely ticketing and labelling our ideas so that we can set them aside or take them up at a moment's notice ; and no better method than that offered by letters and similar signs has yet been devised, whether for the concrete expression of one's own thoughts for one's self, or for written or printed intercommunication beween mind and mind. In chemistry, however, we take care to use formulæ, letters, or symbols (dots, bars, brackets, or what not), only to represent our conceptions respecting real facts—except when we designedly, openly and temporarily use them as a mode of giving rein to the imagination, hoping thereby to be led to inferences which experiments shall prove to be new facts.

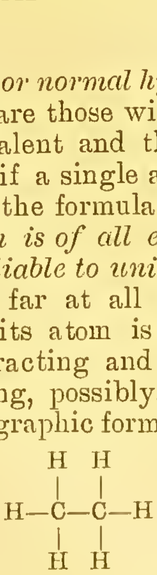
From the consideration of the *composition* and *constitution* of organic compounds we now pass to the subject of *classification.*

HYDROCARBONS: NEUTRAL OR NORMAL, AND BASYLOUS.

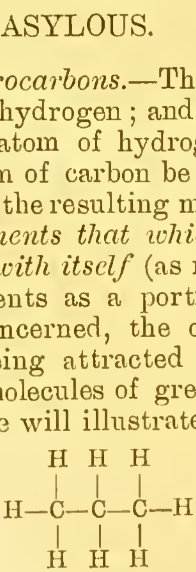
Neutral or normal hydrocarbons.—The simplest compounds of carbon are those with hydrogen ; and as the atom of carbon is quadrivalent and the atom of hydrogen univalent, it follows that if a single atom of carbon be fully saturated with hydrogen, the formula of the resulting molecule must be CH_4. But *carbon is of all elements that which is peculiarly and specially liable to unite with itself* (as magnets attract each other), so far at all events as a portion of the attractive power of its atom is concerned, the other portions of its power attracting and being attracted by other atoms; the result being, possibly, molecules of great complexity. The following graphic formulæ will illustrate this point :—



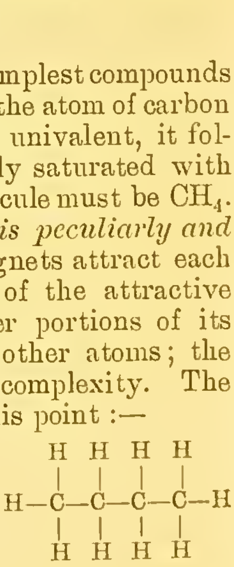
$$H—\underset{H}{\overset{H}{C}}—H$$



$$H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—H$$



$$H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—H$$

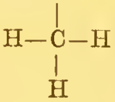


$$H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—H$$

These formulæ represent well-known hydrocarbons, the first being common marsh gas, or methane, one molecule of which is otherwise represented by the shorter formula, CH_4; the next represents ethane, C_2H_6; the third, propane, C_3H_8; while C_4H_{10} is the formula of butane or tetrane. The first three members of the series are gases, those which immediately follow are liquids, C_5H_{12}, C_6H_{14}, etc.; while the highest members are solids, several of which form the mixture of hydrocarbons known as common paraffin; indeed the whole series are distinguished as the *paraffin series* of hydrocarbons. It will be observed that the four units of affinity of the carbon atom are, in the molecule of each substance, fully saturated either by the affinities of adjacent hydrogen atoms, or by that of another carbon atom. The substances are illustrations of *saturated hydrocarbons* (neutral or normal hydrocarbon). They differ in composition by CH_2; add CH_2 to the first, and you obtain the second; add CH_2 to the second, and you obtain the third; and so on. The members of this series resemble each other in containing to a given number of carbon atoms twice that number, with two added, of hydrogen atoms. Representing "any number" by the letter n, the *general* formula for members of this neutral series of hydrocarbons will be C_nH_{2n+2}. Like neutral inorganic salts, their elements have saturated each other's affinities; hence the molecules refuse further to unite by direct or indirect addition with atoms having attractive powers. Potassium is powerfully basylous, chlorine powerfully acidulous, each has great affinity for the other; but the product, chloride of potassium, KCl, is comparatively neutral or normal; saturated hydrocarbons are in the same case, for they do not unite with any other substances.

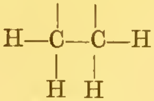
Basylous hydrocarbons.—Many hydrocarbon groups, such as "methyl," CH_3, and "ethyl," C_2H_5, apparently have strong basylous affinities; because, in compounds, they appear to play the part which in inorganic compounds is performed by those basylous metals, etc. (K, Fe, NH_4, *e.g.*) which are commonly called inorganic radicals. Indeed, such hydrocarbon groups are often termed *organic radicals*, and to hold the theory that they exist is convenient; but any attempt to isolate them results in the production of neutral hydrocarbons, C_2H_6, C_4H_{10}, etc.

Some hydrocarbons, however, which can quite easily be isolated, are basylous, such as ethylene, C_2H_4, and other bivalent radicals having the general formula C_nH_{2n}; and acetylene, C_2H_2, and other quadrivalent radicals having the general formula C_nH_{2n-2}. Such radicals are sometimes termed *unsaturated hydrocarbons* :—



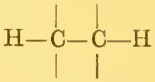
$$\begin{array}{c} | \\ H-C-H \\ | \\ H \end{array}$$

Methyl ?



$$\begin{array}{c} |\quad | \\ H-C-C-H \\ |\quad | \\ H\ \ H \end{array}$$

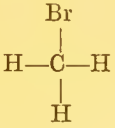
Ethylene ?



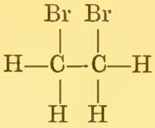
$$\begin{array}{c} |\quad | \\ H-C-C-H \\ |\quad | \end{array}$$

Acetylene ?

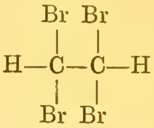
their compounds with, for example, bromine, being thus formulated :—



$$\begin{array}{c} Br \\ | \\ H-C-H \\ | \\ H \end{array}$$

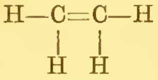


$$\begin{array}{c} Br\ \ Br \\ |\quad | \\ H-C-C-H \\ |\quad | \\ H\ \ H \end{array}$$



$$\begin{array}{c} Br\ \ Br \\ |\quad | \\ H-C-C-H \\ |\quad | \\ Br\ \ Br \end{array}$$

But the first is probably methane in which one atom of hydrogen is substituted by one of bromine, other salts containing the supposed non-isolable radicals being normal hydrocarbons in which atoms of hydrogen are substituted by atoms of acidulous elements or acidulous radicals, the residual hydrocarbon being the so-called basylous radical. And as regards the basylous hydrocarbons which can be isolated, they too probably are neutral hydrocarbons in which the carbon atoms are united to the extent of half or even three-fourths of their affinities, thus :—



$$\begin{array}{c} H-C=C-H \\ |\quad | \\ H\ \ H \end{array}$$

Ethylene.

$H-C\equiv C-H$

Acetylene.

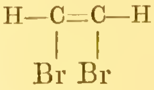
Bring bromine into contact with these so-called free basylous radicals, and, in the case of ethylene, one pair of carbon " arms " may be considered to unclasp, each of the two free arms clasping a one-armed bromine atom ; while, in the case of acetylene, first one pair of arms unclasp and take in two bromine individuals, and then another pair unclasp and take in two more individuals of a bromine molecule.

$Br-Br$

Bromine.

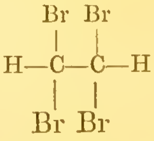
$H-C\equiv C-H$

Acetylene.



$$\begin{array}{c} H-C=C-H \\ |\quad | \\ Br\ \ Br \end{array}$$

Dibromide of acetylene ; or dibrom-ethylene.



$$\begin{array}{c} Br\ \ Br \\ |\quad | \\ H-C-C-H \\ |\quad | \\ Br\ \ Br \end{array}$$

Tetrabromide of acetylene ; or bromide of dibrom-ethylene ; or tetrabrom-ethane.

Molecules.—Instead of the foregoing *plane-conceptions* of molecules, *stereo-conceptions* have been suggested (see p. 464). Thus a tetrahedron may represent a carbon atom, or the area of influence of the (central) carbon atom, its corners or summits representing the foci of its affinities or valencies—foci at which atoms of hydrogen or of compound radicals will find place, or in the vicinity of which they will oscillate. Two or more of such tetrahedra may be regarded as united by their corners, edges, or faces, according to circumstances. This subject cannot be pursued here. Chemists seem to be gliding from statical notions of chemical structure to dynamical ideas, slowly discarding the principle of affinities between fixed particles for that of atoms conditioned by motion. (*See* the memoirs of Van't Hoff, Lebel, Mayer, Guye and others.)

Series of hydrocarbons.—Three distinct series of hydrocarbons have now incidentally been alluded to, namely, the paraffin series, C_nH_{2n+2}; the olefine series, C_nH_{2n}; and the acetylene series, C_nH_{2n-2}. Twelve or fourteen other series are known, as, the terpene series, C_nH_{2n-4}; the benzene series, C_nH_{2n-6}; the cinnamene series, C_nH_{2n-8}; the anthracene series, C_nH_{2n-18}, etc. Each member of any such series obviously differs in composition from the preceding or succeeding member by CH_2. Either series will therefore be an illustration of an *homologous* series (from ὁμὸς, *homos*, the same, and λόγος, *logos*, proportion) of compounds. There will be similar *homology*, of course, between the members of the series of alcohols derived from these hydrocarbons, or between the haloid salts, the ethers, the aldehydes, the acids, etc. Homology is necessarily concurrent with step-by-step variation in the properties of members of a series.

Substitution.—The atoms of hydrogen in any member of either of the series of hydrocarbons may be substituted by radicals of all kinds—basylous and acidulous, elementary and compound; by chlorine or bromine, hydroxyl or sulphydroxyl, oxygen or sulphur, amidogen or imidogen, carboxyl, etc. Very large numbers of organic compounds have thus been obtained artificially; still larger numbers have been proved, analytically, to have distinct existence; while it is certain that still larger numbers exist of which we do not know the constitution and only partially know the composition.

Note.—The idea of substitution, in chemistry, involves or includes the conception of the unity of a molecule as opposed to the old-fashioned conception of duality; involves the unitary conception under which we picture a molecule of, say, anhydrous epsom salt as $MgSO_4$ rather than MgO, SO_3; or, figuratively, involves that conception of oneness or wholeness in a building which allows of one kind of brick being substituted by another kind without change in the structure *quâ* structure. That the idea of substitution also involves, in chemistry, a somewhat unwieldy notation and an extremely unwieldy nomenclature, appears at present to be inevitable.

Procedure as regards further study.

Several of these series of hydrocarbons and their substitutional derivatives will now be described, special notice being given to the compounds of medical and pharmaceutical interest. Some members of the paraffin, olefine, acetylene, terpene, benzene, naphthalene and anthracene series will be treated of, together with their haloid, nitrous, and acetic derivatives, etc.; the alcohols or hydroxyl substitution compounds will then be noticed as a class; and, afterwards, the carbohydrates, amyloids, aldehydes, acids, glucosides, and alkaloids.

The series of chief interest to medical and pharmaceutical and, indeed, to all students, is the first, known by either of the four names *Paraffin*, *Fatty*, *Marsh Gas* or *Methane* Series. The *Benzene* or *Aromatic* Series has great general chemical interest. The *Terpene* Series has considerable pharmaceutical interest.

A very large number of compounds of carbon will thus be brought under notice, far larger than that of any other element. The mere number, however, need not dismay the student. The relation of the derivatives of one hydrocarbon to that hydrocarbon will be found to obtain between the next set of derivatives studied with their hydrocarbon, and so on; hence, as the student progresses, he is soon looking for compounds which he already expects to exist, instead of finding his mind overburdened with what at first sight he might fear would be an intricate and endless subject.

The methods of examining morbid urine will afterwards be experimentally considered. There will then remain to be studied by the medical and pharmaceutical pupil, but by aid of some other guide than the author's, certain galenical, as distinguished from chemical substances, solid and liquid, which can only be fairly regarded from a pharmacist's rather than a chemist's point of view, and a still larger number, doubtless, not yet brought within the grasp of chemist or pharmacist, and of which, therefore, we must at present be content to remain in ignorance. An opportunity, however, will be afforded of noticing the effect of such indefinite organic matter as a vomit, or the contents of a stomach, in masking or preventing the reactions by which mineral and vegetable poisons are detected.

A section on quantitative analysis will complete the Manual.

QUESTIONS AND EXERCISES.

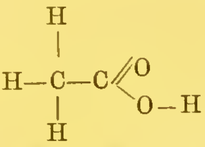
What do you understand by organic chemistry?—Give methods of ascertaining the presence of carbon, hydrogen, and nitrogen in organic compounds.—Give an outline of the methods by which the quantities of carbon, hydrogen, oxygen, and nitrogen are determined in organic compounds.—How would you convert centesimal into "atomic" composition? —Define *empirical*, *molecular*, and *rational* formulæ.—How is the constitution of an organic compound ascertained?—What do you understand by graphic chemical formulæ?—Define "stereo-chemical" formulæ.—Give graphic formulæ of two or three saturated hydrocarbons.—What do you mean by an organic radical?—Give illustrations.—Give the general formulæ of different series of hydrocarbons, with special illustrations.—Define *substitution*, as understood in organic chemistry.

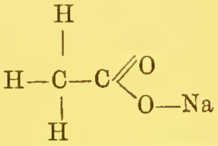
THE PARAFFIN SERIES OF HYDROCARBONS.

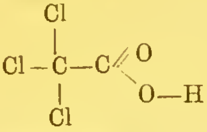
METHANE. *Marsh gas. Light carburetted hydrogen. Hydride of methyl. Fire-damp.* CH_4.—This gaseous hydrocarbon may be made from its elements by uniting the carbon with sulphur and the hydrogen with sulphur or oxygen, and passing these over red-hot copper. It occurs naturally in coal mines and in the mud-volcanoes of the Crimea, is frequently associated with the crude petroleum that issues from the earth, and is constantly rising in bubbles to the surface of stagnant pools in marshy places. It is a non-luminous constituent of ordinary coal gas. It is inodorous and colourless. It may be produced by acting on iodide of methyl with zinc on which copper has been deposited, and in other theoretically interesting ways, but economically by heating a mixture of 2 parts of dry acetate of sodium, 3 of lime, and 2 of caustic soda or, better, potash.

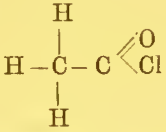
$$\underset{\text{Acetate of sodium.}}{CH_3{\cdot}CO{\cdot}ONa} + \underset{\text{Soda.}}{NaOH} = \underset{\text{Methane.}}{CH_4} + \underset{\text{Carbonate of sodium.}}{CO_3Na_2}.$$

Two notes on the notation of the foregoing and similar formulæ, and on the constitution of salts.—(*a*) Soda, NaHO, contains bivalent oxygen, univalent sodium, and univalent hydrogen. The chemical valency of the oxygen atom is double that of either of the other atoms, a relationship perhaps better realized if the symbol for the oxygen be placed between those of hydrogen and sodium, NaOH, or HONa. So HOK, HOH, etc. The student must expect to find the symbols of a formula placed where apparently they will best reflect our knowledge of the structure of the molecule pictured. (*b*) Acetic acid, $C_2H_4O_2$, by action of chlorine (presented as PCl_3) loses hydroxyl, OH, and yields chlorine of acetyl, C_2H_3OCl. Hence acetic acid would seem in constitution to be hydrate of acetyl, $C_2H_3O{\cdot}OH$; especially when we find that the chloride of acetyl by reaction with water, HOH, yields again acetic acid (and HCl). Sodium will only displace one atom of hydrogen from water, yielding HONa; and will only displace one atom of hydrogen from acetic acid, yielding acetate of sodium, $C_2H_3O{\cdot}ONa$. Further, chlorine will not displace more than one portion or atom of hydroxyl, OH, from acetic acid. So that three atoms of the hydrogen in acetic acid apparently perform different functions to those of the fourth atom; and, apparently, the two atoms of oxygen perform different functions. Hence our necessity for separating in the formula the letters representing those atoms, $C_2H_3O{\cdot}OH$. Once more, acetates may be formed from two different methyl compounds: acetate of sodium by the direct combination of methide of sodium, CH_3Na, and carbonic acid gas, CO_2, giving $CH_3{\cdot}CO{\cdot}ONa$; and acetate of ammonium by the combination of methyl cyanide, CH_3CN, with water (2HOH), yielding $CH_3{\cdot}CO{\cdot}ONH_4$. From these and other facts and modes of reasoning arise our justification—from them, indeed, come the necessity—for thus extending the formulæ for acetates. Less extended formulæ are of course correct and even occasionally more useful; $C_2H_4O_2$ $C_2H_3O_2H$, $C_2H_3O{\cdot}OH$, $CH_3{\cdot}CO{\cdot}OH$ form an illustration of a set of formulæ for a substance either member of which set may be used according to circumstances. (*See* also pages 333 and 350.) The following would be reasonable *graphic* formulæ, like those on page 464 or 466 :—


Acetic acid.


Acetate of sodium.


Trichloracetic acid.


Chloride of acetyl.

ETHANE, C_2H_6. *Dimethyl. Hydride of Ethyl.*—This is one of the constituents of crude petroleum. It also results on heating iodide of ethyl with granulated zinc or zinc covered with copper, and then adding water to the iodide of zinc and ethide of zinc first produced.

$$2Zn + 2C_2H_5I = Zn(C_2H_5)_2 + ZnI_2$$
$$Zn(C_2H_5)_2 + 2OH_2 = 2C_2H_6 + Zn(OH)_2$$

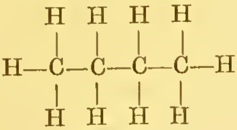
Ethane is sometimes regarded as dimethyl or methylmethane, CH_3CH_3, that is to say, as being derived from methane by the substitution of an atom of hydrogen in methane, CH_4, by methyl, CH_3; its properties, however, are not those of a radical. It is also considered to be hydride of ethyl, C_2H_5H; its properties, however, are not those of such a substance. The other hydrocarbons of the paraffin series are also similarly regarded as containing radicals. Such views of constitution are useful as enabling composition to be remembered and relationships to be realized, especially if their hypothetical character be fully recognised; but these hydrocarbons are apparently single homogeneous substances, and whatever other views of their constitution be held, this last should be dominant.

PROPANE, *methyl ethyl*, C_3H_8.—This gas, like methane occurs dissolved in the Pennsylvanian petroleum springs.

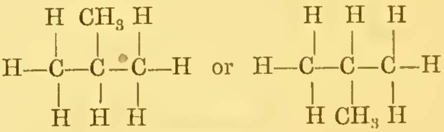
TETRANE or BUTANE, C_4H_{10}.—Two varieties exist, *normal butane* or *diethyl*, $C_2H_5{\cdot}C_2H_5$, found in petroleum, and *iso-*

butane or *trimethyl methane*, $CH(CH_3)_3$ formed by artificial means.

Turning back to the highly extended formulæ for methane, ethane, propane, and butane given on p. 466, the reader will see why there should only be one ethane or propane while two butanes (two methyl-propanes) are possible. We can but replace one of the atoms of hydrogen, H, in methane, CH_4, to form ethane, $CH_3{\cdot}CH_3$, and it matters not which, hence only ethane (one ethane) can result. In ethane, $CH_3{\cdot}CH_3$, if an atom of hydrogen be displaced by methyl, CH_3, it can but be a hydrogen atom of one of the two methyl groups ($CH_3{\cdot}CH_3$), and it matters not which (though two *di*-derivatives may exist; see the respective chlorides of ethylene and ethylidene, p. 490). But in propane, $CH_3{\cdot}CH_2{\cdot}CH_3$, a CH_2 group exists as well as CH_3 groups. Now CH_2 is a different group to CH_3, hence if we displace one of its two atoms of hydrogen (it matters not which) by methyl to get butane, we should expect to get a butane of different properties to the butane obtained by displacing one of the atoms of hydrogen in the methyl groups by methyl; and two butanes, and two only, do actually exist. Normal butane may be thus formulated, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, while isobutane would be either, $CH_3{\cdot}CH_3{\cdot}CH{\cdot}CH_3$, or a practically identical formula $CH_3{\cdot}CH{\cdot}CH_3{\cdot}CH_3$.



Butane.



Isobutane.

PENTANE, C_5H_{12}.—Three varieties are possible, and three only; three are known, and three only; the second, or *isoamylic hydride*, yielding the ordinary Amylic Alcohol and Valerianic Acid.

HEXANES, C_6H_{14}.—Five are possible, five are known.

HEPTANES, C_7H_{16}.—Nine are possible, five are known.

OCTANES, C_8H_{18}.—Eighteen isomers possible, three known.

NONANE, C_9H_{20}; DECANE, $C_{10}H_{22}$; and every paraffin hydrocarbon up to $C_{24}H_{50}$, as well as some others and derivatives of far higher members of the paraffin series of hydrocarbons, are known.

Petroleum Spirit. Paraffin Oil. Paraffin.

Petroleum Spirit, B.P. (*pentane*, C_5H_{12}, *hexane*, C_6H_{14}, etc.), known also as *benzoline*, *petroleum benzin*, and *petroleum ether* is "a colourless, very volatile, and highly inflammable liquid obtained from petroleum, and consisting of a mixture of the lower members of the paraffin or marsh-gas series of hydrocarbons. Boiling-point, 122° to 140° F. (50° to 60° C.). Specific gravity, about 0·670 to 0·700." (Benzene or benzol is quite a different fluid, *vide* Index.)

Paraffin Oil, the *Paraffinum Liquidum* of the German Pharmacopœia, is a mixture of the higher fluid members of the paraffin series of hydrocarbons, a clear oily liquid obtained from petroleum after distilling off the lower-boiling portions. Specific gravity, not below 0·840. Boiling-point, not below 360° C. (680° F.). Digested and agitated with warm sulphuric acid for a day or two, the oil is not coloured and the acid only tinged brown; metallic sodium under similar conditions is not tarnished; alcohol boiled with the oil should not become acid. *Soft Paraffin* (*Paraffinum Molle*, B.P.), officially termed *Unguentum Paraffini* in Germany, *Pétroléine* in France, and *Petrolatum* in the United States, and "known in commerce by various fanciful names," is a semi-solid mixture of paraffins, usually obtained by purifying the less volatile portions of petroleum. It is "white or yellowish, translucent, soft, greasy; free from acidity, alkalinity, or any unpleasant odour or flavour, even when warmed to 120° F. (48·9° C.). Specific gravity at the melting point from about 0·840 to 0·870. Melts at 95° to 105° F. (35° to 40·5° C.), or even somewhat higher; volatilizes without giving acrid vapours, and burns with a bright flame, leaving no residue. Insoluble in water, slightly soluble in absolute alcohol, freely soluble in ether, chloroform, benzol, etc. It is not saponified by solutions of alkalies." *Hard Paraffin* (*Paraffinum Durum*, B.P.), commonly termed *paraffin wax*, or simply *paraffin*, is "a mixture of several of the harder members of the paraffin series of hydrocarbons; usually obtained by distillation from shale, separation of the liquid oils by refrigeration, and purification of the solid product. It is colourless, semi-transparent, crystalline, inodorous, and tasteless; slightly greasy to the touch. Specific gravity, 0·82 to 0·94. Insoluble in water, slightly soluble in absolute alcohol, freely soluble in ether. It melts at 110° to 145° F. (43·3° to 62·8° C.), and burns with a bright flame, leaving no residue."

Paraffin resists all ordinary reagents (hence the original name *paraffin*, from *parum affinis*, without affinity), but may, by continued boiling with sulphuric acid and solution of bichromate of potassium, be oxidized to *cerotic acid*, $C_{27}H_{54}O_2$, and by continued digestion with nitric and sulphuric acids yields acids of the acetic series and *paraffinic acid*, $C_{24}H_{48}O_2$ (Pouchet).

SUBSTITUTION-PRODUCTS OF METHANE.—The paraffins all form substitution derivatives with the halogens, chlorine acting energetically, bromine less so, and iodine scarcely at all. In the preparation of chlorine and bromine substitution-products by acting on the hydrocarbons, the mono-derivatives are always mixed with the higher derivatives, even though the quantities are taken in relation to their combining proportions; thus, if methane and chlorine are mixed in the proportion of $CH_4 + Cl_2$, not only will *monochloromethane*, or *chloride of methyl*, CH_3Cl, be formed, but *dichloromethane*, CH_2Cl_2, and *trichloromethane*, $CHCl_3$ with free hydrogen. The best method of obtaining the mono-derivatives is to act on the alcohols by haloid acids or by phosphorus compounds:—

$$CH_3OH + HCl = CH_3Cl + H_2O$$
$$3CH_3OH + PCl_3 = 3CH_3Cl + PH_3O_3.$$

Chloroform.

Trichloromethane or *chloroform*, $CHCl_3$ may be made by acting on methane with chlorine, as already indicated:—

$$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$$

also as shown on p. 479; but on a larger scale by the official process, as follows:—

Process.—One fluid ounce and a half of spirit and 24 of water are placed in a retort or flask of at least a quart capacity; 8 ounces of chlorinated lime and 4 of slaked lime are added, the vessel connected with a condenser, and the mixture heated until distillation commences, the source of heat then being withdrawn. The condensed liquid should fall into a small flask containing water, at the bottom of which about a drachm of chloroform will slowly collect.

Explanation of the Process.—Though there is some doubt as to the exact reaction, the following seems to be most probable. The hypochlorite of calcium believed to be present in the chlorinated lime (*see* the remarks in connection with the latter, p. 125) readily yields up oxygen and chlorine to organic substances, the calcium being liberated as hydrate. The alcohol used in making chloroform is thus probably first converted into aldehyde*:—

$$\underset{\text{Alcohol.}}{2CH_3\cdot CH_2OH} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyde.}}{2CH_3COH} + \underset{\text{Water.}}{2H_2O}$$

The action of chlorine on aldehyde then probably gives chloral (*chlor-al*dehyde):—

$$\underset{\text{Aldehyde.}}{CH_3\cdot COH} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{CCl_3\cdot COH} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

The hydrochloric acid being at once neutralized by some of the liberated hydrate of calcium to form chloride of calcium and water, more freed hydrate of calcium and chloral give formate of calcium and chloroform.

$$\underset{\text{Chloral.}}{2CCl_3\cdot COH} + \underset{\text{Hydrate of calcium.}}{Ca2HO} = \underset{\text{Formate of calcium.}}{(HCOO)_2Ca} + \underset{\text{Chloroform.}}{2CHCl_3}$$

Or, irrespective of the chemistry of each step in the process, and regarding only the materials and the products, 4 molecules of alcohol and 8 of hypochlorite of calcium give 2 of chloroform, 3 of formate of calcium, 5 of chloride of calcium, and 8 of water, thus:—

$$\underset{\text{Alcohol.}}{4CH_3CH_2OH} + \underset{\text{Calcium hypochlorite.}}{8CaCl_2O_2} =$$

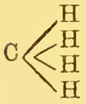
$$\underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium formate.}}{3(H\cdot COO)_2Ca} + \underset{\text{Calcium chloride.}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}$$

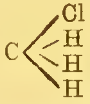
---

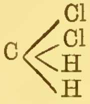
* The special formulæ for alcohol, aldehyde, and the formate used in the accompanying equations will be better understood when the constitution of alcohols and acids has been considered.

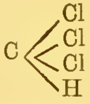
The hydrate of calcium placed in the generating-vessel is not essential, but is useful in preventing secondary decompositions, the hydrate of calcium obtainable from the reaction being insufficient for this purpose.

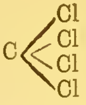
Chlorine converts chloroform into *tetrachloromethane* or *tetrachloride of carbon*, CCl_4, completing the chlorine substitution-products of methane.


Methane.


Monochloromethane.


Dichloromethane.


Trichloromethane (Chloroform).


Tetrachloromethane. (Carbon tetrachloride).

Chloroform is purified by shaking it with water and then with pure sulphuric acid (containing no trace of nitric acid), which chars and removes hydrocarbons, etc., but does not affect chloroform. It is freed from any trace of acid by agitation with lime, and from moisture by solid chloride of calcium. It is finally rectified.

Properties.—The sp. gr. of pure chloroform is at least 1·500, perhaps higher. It is liable to slowly decompose when exposed to air and light; $4CHCl_3 + 3O_2 = 4COCl_2 + 2H_2O + 2Cl_2$. The resulting chlorine may be detected by iodide of zinc and starch and the oxychloride of carbon by baryta water; $2COCl_2 + 2H_2O = 2CO_2 + 4HCl$. To render it stable a minute amount (1 volume in 100 or less) of absolute alcohol is necessary: hence the specific gravity of medicinal chloroform is about 1·497. It readily and entirely volatilizes at common temperatures, having, to the last drop, its pleasant characteristic odour. It has a sweetish taste, is limpid, colourless, soluble in alcohol and ether, and slightly in water. It may be so frozen at low temperatures that any impurities shall remain in the still fluid portion (Pictet). Boils at 142° F. It burns with a sluggish, green, smoky flame. It reduces Fehling's solution. It should be neutral to test-paper, indicating absence of acid; give no precipitate with solution of nitrate of silver, indicating absence of ordinary chlorides; remain colourless when heated with potash, indicating absence of aldehyde; and give no more colour than is producible by the absolute alcohol that is present to any sulphuric acid with which it may be shaken, even after the mixture has been set aside for half an hour, indicating absence of hydrocarbons, etc. Alcohol may be detected by the iodoform test (*see* Index), or by shaking with a little of the dye termed "Hofmann's violet," which gives the chloroform a purple tint if alcohol be present, but affords no colour with pure chloroform. At the temperature of melting ice, chloroform unites with water to form a crystalline compound, $CHCl_3, 18H_2O$.

Aqua Chloroformi, B.P., the official Chloroform Water is made by shaking 1 fluid drachm of chloroform with 25 ounces of distilled water till dissolved.

Iodoform.

Tri-iodomethane or *iodoform*, CHI_3, analogous in constitution to chloroform, the iodine occupying the place of the chlorine, is made by mixing together one part of alcohol, two parts of crystallized carbonate of sodium, and ten parts of water; the whole being heated to about 150° F., and one part of iodine gradually added in small portions. When the fluid becomes colourless, the iodoform is allowed to settle. The iodoform is collected on a filter, washed thoroughly with water, and dried between filtering-paper. (This reaction forms a very delicate means of testing the presence of alcohol. *Vide* "Alcohol, Test for," in Index.)

Iodoform occurs as yellow, shining, six-sided scales. It is volatile at ordinary temperatures. Almost insoluble in water, soluble in alcohol or ether. Warmed with an alcoholic solution of potash, formate and iodide of potassium are produced, $CHI_3 + 4KOH = HCOOK + 3KI + 2H_2O$; and the resulting fluid, heated with a little nitric acid, yields free iodine, recognised by its colour or by giving a blue colour with starch.

Chloroform, *iodoform*, and *bromoform* may also be obtained on passing a current of electricity through hot strong alcohol containing chloride, iodide, or bromide of potassium, respectively, carbonic anhydride being simultaneously supplied; or again by the action of bleaching powder, or a mixture of chlorinated soda with bromide or iodide of potassium, on acetone. The latter "*ketone chloroform*" is a commercial article.

SUBSTITUTION - PRODUCTS OF ETHANE.—Ethane, like methane, yields substitution derivatives. *Monobromethane*, *bromide of ethyl*, *ethylic bromide*, or *hydrobromic ether*, C_2H_5Br, may be prepared by gradually adding 6 parts of bromine to a mixture of six parts of ethylic alcohol and 1 of amorphous phosphorus contained in a flask fitted with an upright condenser, care being taken to keep the apparatus cool.

$$5C_2H_5OH + PBr_5 = 5C_2H_5Br + H_3PO_4 + H_2O.$$

When all the bromine has been added, the mixture is poured into a retort and distilled over a water-bath, the resulting ethylic bromide freed from excess of bromine by washing with a small quantity of dilute soda or potash, then washed with water and rectified over calcium chloride and redistilled.

For its preparation on a large scale, De Vrij's method [illegible] preferable, $C_2H_5HSO_4 + KBr = C_2H_5Br + KHSO_4$ (*see Pharm. Journ.*, Feb. 15, 1879), or the same method as modified by Greene (*P. J.*, July 12, 1879); by Remington (*P. J.*, May 29, 1880); or by Wolff (*P. J.*, July 3, 1880).

Mon-iodoethane, *iodide of ethyl*, or *ethylic iodide*, C_2H_5I, may be made, like the bromide, by mixing 7 to 8 parts of amorphous phosphorus and 70 of absolute alcohol with 100 parts of iodine. The complete decomposition takes three or four hours, after which it may be treated as above. It should be kept in a dark place, as light favours decomposition and liberation of iodine.

The paraffins give rise to many substitution derivatives by displacement of their hydrogen by compound acidulous radicals. The following, chiefly from ethane and pentane, are of pharmaceutical interest:—

Spirit of Nitrous Ether.

Nitrite of Ethyl, *Nitrous Ether*, $C_2H_5NO_2$.—A "spirit," probably containing nitrous ether, was one of the earliest known medicinal compounds, its discovery being generally ascribed to Raymond Lully.

Process.—To a third of a test-tubeful of rectified spirit add about a tenth of its bulk of sulphuric acid, rather more of nitric acid, and some copper wire or turnings, and warm the mixture; as soon as ebullition commences, the vapour of nitrous ether (with other substances) is evolved, recognised by its odour. A long bent tube, kept very cool, may be adapted by a perforated cork to the test-tube, and thus a little of the product be condensed and collected.

The above process conducted on a larger scale, with definite quantities of materials, temperature regulated by a thermometer, and a well-cooled condenser, etc. (*see* p. 141), is the official process (Kopp's process applied by Redwood) for the preparation of a concentrated solution of nitrous ether, etc., in spirit; diluted with nearly three times its bulk of rectified spirit, it forms the official variety of the "spirit of nitrous ether" (*Spiritus Ætheris Nitrosi*, B.P.) of pharmacy.

"Take of—

Nitric Acid	3 fluid ounces,
Sulphuric Acid	2 fluid ounces,
Copper, in fine wire, (about No. 25)	2 ounces,
Rectified Spirit	a sufficiency.

"To one pint of the spirit add gradually the sulphuric acid, stirring them together; then add, in the same way, two and a half fluid ounces of the nitric acid. Put the mixture into a retort or other suitable apparatus, into which the copper has been introduced, and to which a thermometer is fitted. Attach now an efficient condenser, and, applying heat gently, let the spirit distil at a temperature commencing at 170° F. and rising to 175°, but not exceeding 180°, until twelve fluid ounces have passed over and been collected in a bottle kept cool, if necessary, with ice-cold water; then withdraw the heat, and having allowed the contents of the retort to cool, introduce the remaining half-ounce of nitric acid, and resume the distillation as before, until the distilled product has been increased to fourteen fluid ounces. Mix this with two pints of the rectified spirit, or as much as will make the product correspond to the official test (*vide infra*). Preserve it in thoroughly well-closed vessels."

Disregarding the other products, the following equation probably represents the chief decompositions that occur in the operation. An important feature in the reaction is the reduction of the nitric to the nitrous radical by the indirect agency of the copper.

$$\underset{\text{Alcohol.}}{3C_2H_5OH} + \underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Copper.}}{Cu}$$

$$= \underset{\text{Nitrous ether.}}{2C_2H_5NO_2} + \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Sulphate of copper.}}{CuSO_4}$$

Properties.—Spirit of Nitrous Ether "is transparent and nearly colourless, with a very slight tinge of yellow, mobile, inflammable, of a peculiar penetrating apple-like odour, and sweetish cooling sharp taste. Specific gravity (B.P.) 0·840 to 0·845. It does not effervesce, or only feebly when shaken with a little bicarbonate of sodium" (showing absence of appreciable quantities of free nitrous, acetic or other acids). The aldehyde in it may be detected by the potash test (*see* "Aldehyde, Test for" in Index). The great tendency of aldehyde to become converted into acetic acid by the absorption of oxygen from the air renders Spirit of Nitrous Ether unstable, and pharmacists are obliged to neutralize such acid, generally by bicarbonate of potassium, before adding it to medicines containing iodides, etc.

A very old variety of spirit of nitrous ether, or rather "sweet spirit of nitre," still largely sold in Great Britain, is made from spirit of wine and nitric acid, as ordered in the London Pharmacopœias, except that the distillation is continued until the product has a sp. gr. of 0·850. It may contain little or no nitrite, but is popular.

Test.—Any nitrous radical may be detected by adding sulphate of iron and sulphuric acid to some of the spirit of nitrous ether, the usual black compound being produced.

Official (B.P.) *test of strength.*—"Tested as described in the *Pharmaceutical Journal*, 3rd series, vol. xiii. p. 63 [Eykman's test]; or vol. xv. p. 101 [Dymond's modification of Eykman's apparatus]; or vol. xv. p. 673 [Allen's modification], it should yield, at the ordinary temperature (60° F., 15·5° C.) and pressure (30 inches, or 760 millimetres of mercury), and when freshly prepared, seven times its volume of nitric oxide gas: and even after it has been kept some time and the vessel containing it has occasionally been opened, it should yield not much less than five times its volume of the gas." The operation is simple. A given volume of the spirit is run into any ordinary *nitrometer* charged with brine, a solution of iodide of potassium added, and then diluted sulphuric acid. When the gas ceases to collect, it is measured.

$$C_2H_5NO_2 + KI + H_2SO_4 = C_2H_5OH + KHSO_4 + I + NO.$$

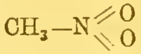
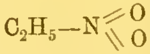
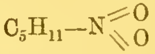
If the gas were yielded by nothing but nitrite of ethyl, the seven volumes would correspond to nearly 3 per cent. of that substance, and the five volumes to nearly 2 per cent.

For the detection of methyl alcohol in spirit of nitrous ether, *vide* "Methylated Sweet Spirit of Nitre" in Index.

Pure Nitrite of Ethyl.—Dr. Leech states that the physiological and the therapeutic action of "spirit of nitrous ether" is similar to that of an alcoholic solution of nitrite of ethyl of similar nitrous strength. The nitrite was prepared for Dr. Leech in the Research Laboratory of the Pharmaceutical Society of Great Britain, by Hare's process of mixing nitrite of sodium, sulphuric acid, and alcohol at a low temperature—but, perhaps for the first time, in a pure condition. The nitrite separates as a pale yellow layer. It may be washed rapidly with a little water and dried with anhydrous carbonate of potassium. As it is decomposed by prolonged contact with water, Dr. Leech was supplied, according to suggestions and experiments by the late John Williams, with a pure solution of the ether in absolute alcohol containing five per cent. of glycerine as a preservative. It should be dispensed and used from small bottles to avoid loss by volatilization and to prevent absorption of moisture from the air.

$$\underset{\substack{\text{Nitrite of}\\ \text{sodium.}}}{2NaNO_2} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Hydrate}\\ \text{of ethyl.}}}{2C_2H_5OH} = \underset{\substack{\text{Nitrite of}\\ \text{ethyl.}}}{2C_2H_5NO_2} + \underset{\substack{\text{Sulphate}\\ \text{of sodium.}}}{Na_2SO_4} + \underset{\text{Water.}}{2H_2O}$$

Nitro-compounds.—There are two nitro-ethylic compounds having similar composition but differing very much in properties, namely, *nitrite of ethyl* ($C_2H_5NO_2$), which boils at 63·5° F. (17·5° C.) and has a sp. gr. of 0·900 (at 0° C.; water = 1; 0·917 to 0·920; Dunstan and Dymond) and *nitro-ethane* ($C_2H_5NO_2$) which boils at about 235° F. (nearly 113° C.) and has a sp. gr. of 1·058. There are also two nitro-methylic compounds, namely, nitrite of methyl (CH_3NO_2) and nitromethane (CH_3NO_2). The nitrites are easily decomposed, the nitro-compounds are stable. The official spirit of nitrous ether contains nitrite of ethyl. Possibly the nitrites contain the nitrogen in the trivalent or unsaturated condition, while in the nitro-compounds it is in the quinquivalent or saturated state. Moreover, the reaction of the two sets of bodies warrant the conclusion that in the nitrites the methyl or ethyl is united to oxygen, in the nitro-compounds to the nitrogen. Each hydrocarbon furnishes only one mono-nitrite; each hydrocarbon furnishes only one mono-nitro compound. The nitrites are, the nitro-compounds are not, saponifiable; on reduction, the nitrogen of the former does not, while that of the latter does, remain with the radicals, yielding amines. There are two similar nitro-amylic compounds.

Nitrite of methyl,	$CH_3—O—N=O$.	Nitro-methane,	 $CH_3—N\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix}$
Nitrite of ethyl,	$C_2H_5—O—N=O$.	Nitro-ethane,	 $C_2H_5—N\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix}$
Nitrite of amyl,	$C_5H_{11}—O—N=O$.	Nitro-pentane,	 $C_5H_{11}—N\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix}$

Acetic Ether, or Acetate of Ethyl.

Acetate of Ethyl, or *Acetic Ether* $CH_3{\cdot}CO{\cdot}OC_2H_5$, or $C_2H_5C_2H_3O_2$.—To a little dried acetate of sodium, in a test-tube, add a small quantity of rectified spirit of wine and some sulphuric acid. Adapting a long bent tube in the usual manner, heat the test-tube and so distil over acetic ether—which may be collected in another test-tube kept cool by partial immersion in cold water.

The official proportions (*Æther Aceticus*, B.P.) are: rectified spirit, 32¼ fluid ounces; sulphuric acid, 32½ fluid ounces; acetate of sodium, 40 ounces; carbonate of potassium, freshly dried, 6 ounces. To the spirit slowly add the acid, keeping the fluid cool, and the product being cold, add the acetate, mixing thoroughly. Distil forty-five fluid ounces. Digest the distillate with the carbonate of potassium for three days in a stoppered bottle. Separate the ethereal fluid, and again distil until all but about four fluid ounces have passed over. Preserve the resulting acetic ether in a well-closed bottle and in a cool place. It is a colourless liquid with an agreeable ethereal odour. Specific gravity, about 0·900. Boiling point, about 166° F. (74·4° C.). Soluble in all proportions in rectified spirit and in ether. One part, by weight, dissolves in about 10 parts of water at 60° F. (15·5° C.).

$$\underset{\substack{\text{Hydrate of}\\\text{ethyl.}}}{C_2H_5OH} + \underset{\substack{\text{Acetate of}\\\text{sodium.}}}{CH_3{\cdot}CO{\cdot}ONa} + \underset{\substack{\text{Sulphate of}\\\text{hydrogen.}}}{H_2SO_4}$$

$$= \underset{\substack{\text{Acetate of}\\\text{ethyl.}}}{CH_3CO{\cdot}OC_2H_5} + \underset{\substack{\text{Sulphate of sodium}\\\text{and hydrogen.}}}{NaHSO_4} + \underset{\substack{\text{Hydrate of}\\\text{hydrogen.}}}{HOH}$$

Acetate of Amyl, $CH_3{\cdot}CO{\cdot}OC_5H_{11}$, or $C_5H_{11}C_2H_3O_2$. (Fousel oil, or ordinary amylic alcohol, is a mixture of two or more alcohols derived from pentane, but the derivatives may be simply termed amyl compounds; *vide* Pentylic or Amylic Alcohol in Index.)

To a small quantity of amylic alcohol in a test-tube add some acetate of potassium and a little sulphuric acid, and warm the mixture; the vapour of acetate of amyl is evolved, recognised by its odour, which is that of the jargonelle pear. If a condensing tube be attached, the essence may be distilled over, washed by agitation with water, to free it from alcohol, and separated by a pipette.

$$\underset{\substack{\text{Acetate of}\\\text{potassium.}}}{CH_3{\cdot}CO{\cdot}OK} + \underset{\substack{\text{Amylic}\\\text{alcohol.}}}{C_5H_{11}OH} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

$$= \underset{\substack{\text{Acetate of}\\\text{amyl.}}}{CH_3{\cdot}CO{\cdot}OC_5H_{11}} + \underset{\substack{\text{Acid sulphate}\\\text{of potassium.}}}{KHSO_4} + \underset{\text{Water.}}{H_2O}$$

Fruit-essences.—Acetate of amyl, prepared with the proper equivalent proportions of constituents, as indicated by the above equation, is largely manufactured for use as a flavouring agent by confectioners. Valerianate of amyl ($C_5H_{11}C_5H_9O_2$) is similarly used under the name of apple-oil. Butyrate of ethyl ($C_2H_5C_4H_7O_2$) closely resembles the odour and flavour of pine-apple; œnanthylate of ethyl ($C_2H_5C_7H_{13}O_2$) recalls greengage; pelargonate of ethyl ($C_2H_5C_9H_{17}O_2$) quince; suberate of ethyl ($C_2H_5C_8H_{12}O_4$) mulberry; sebacate of ethyl ($C_2H_5C_{10}H_{16}O_4$) melon. Salicylic aldehyde (the old salicylol or salicylous acid), $C_6H_4{\cdot}OH{\cdot}COH$, is the essential oil of meadow sweet (*Spiræa ulmaria*), and may be prepared artificially by the oxidation of salicin (*vide* Index "Salicin"). Acid salicylate of methyl ($CH_3HC_7H_4O_3$), or gaultheric acid, forms the chief part of the essential oil of winter-green (*Gaultheria procumbens*, the fresh leaves of which yield about 0·4 per cent. of oil). Oil of sweet birch (*Betula lenta*) is salicylate of methyl. Salicylic aldehyde may also be prepared artificially by heating chloroform and sodium phenol. Salicylic acid ($C_6H_4\cdot OH\cdot COOH$) can be obtained from the salicylate of methyl, but more cheaply from carbolic acid.

By mixing such *ethereal salts* (*alkyl salts* or *esters; vide* Index) with each other and with essential oils in various proportions, the odour and flavour of nearly every fruit may be fairly imitated. (For a set of formulæ of fruit-essences, *see Pharmaceutical Journal*, May 17, 1879).

Nitrite of Amyl.

Nitrite of Amyl (*Amyl Nitris*, B.P.) ($C_5H_{11}NO_2$). This may be prepared on the large scale by the direct action of nitric acid on amylic alcohol, the nitric acid being reduced to nitrous by a portion of the alcohol, and valerianic aldehyd with valerianic acid being produced. The heat must be very carefully regulated, or the reaction may become extremely violent; indeed, with small quantities a violent explosion may occur. For experimental purposes it is preferable to pass nitrous gases, generated by the action of nitric acid on white arsenic or on starch, into the amylic alcohol (kept cool by standing the vessel in cold water) until the alcohol is saturated. The product is shaken with an aqueous solution of hydrate or carbonate of potassium to remove free acids, and the oily liquid then separated and distilled. The portion distilling between 205° F. and 212° F. is the nitrite of amyl.

The official nitrite of amyl is a yellowish ethereal liquid; sp. gr. of liquid 0·902, of vapour 4·03; boiling-point, 205° F.; soluble in spirit of wine, insoluble in water; converted by fused caustic potash into valerianate of potassium: exposed to the air, it yields amylic alcohol. If of good quality (for physiological purposes, although perhaps not chemically pure), about 70 per cent. will distil between 194° and 212° F. (90° to 100° C.), the bulb of the thermometer being in the vapour and not touching the residual fluid.

The official and commercial varieties of "nitrite of amyl" are well known to be only "chiefly" (B.P.) real nitrite of amyl. Since the British Pharmacopœia was published, the staff of the Research Laboratory of the Pharmaceutical Society have shown that the fluid may contain the nitrites of both alpha-amyl and beta-amyl, nitrite of iso-butyl, and nitrite of propyl, and have furnished specimens of these substances to Professor Cash, who finds that their physiological action is not primarily dependent on the amount of their nitrosyl. These nitrites are, of course, derived from the corresponding hydrates (see pp. 534 and 535) present in the amylic alcohol.

Nitropentane ($C_5H_{11}NO_2$) is similar to nitrite of amyl in composition, but differing much in properties. It is obtained by reaction of iodide of amyl on nitrite of silver. It boils at 300° to 320° F. For remarks made respecting the two similar derivatives of ethane, *see* page 483.)

QUESTIONS AND EXERCISES.

How would you prepare methane and ethane? Give formulæ.—Give details of the production of chloroform from alcohol, tracing the various steps by equations.—Give the formulæ and state the constitution of the various chlorine derivatives of methane.—How is chloroform purified?—State the characters of pure chloroform.—Explain the official process for the preparation of nitrous ether.—Give the properties of nitrous ether as compared with nitro-ethane.—By what official method is the strength of spirit of nitrous ether to be estimated?—How is iodide of ethyl made?—Mention the systematic names of several artificial fruit-essences.—What is the formula of nitrite of amyl, and how is it prepared?

THE OLEFINE SERIES OF HYDROCARBONS.

The Olefine series of Hydrocarbons consists of *unsaturated* hydrocarbons, having the general formula, C_nH_{2n}. *Ethylene*, C_2H_4; *Propylene*, C_3H_6; *Butylene*, C_4H_8; *Amylene*, C_5H_{10}; *Hexylene*, C_6H_{12}; and *Heptylene*, C_7H_{14}; and many others are well known.

Ethylene, *Olefiant Gas*, or *Heavy Carburetted Hydrogen*, C_2H_4, is the first of this series. It is formed in the destructive distillation of coal, and is the chief illuminating constituent of coal-gas. Coal gas consists of 30 to 40 per cent. of methane, 40 to 50 per cent. of hydrogen, and from 5 to 7 per cent. of ethylene and its homologues. Hydrocarbons, normally fluid but kept in the vaporous condition by the diluents, also contribute materially to the illuminating power of gas. The impurities are nitrogen, air, carbolic acid, bisulphide of carbon (CS_2) and some badly smelling sulphur compounds. Upwards of 150 distinct chemical substances have been obtained from the solid, liquid, and gaseous products of the destructive distillation of coal.

Preparation.—Ethylene may be prepared by dropping alcohol into a large retort or flask containing 10 ounces of sulphuric acid and 3 ounces of water heated to 160–165° C. The gas is washed in cold water and a solution of soda to free it from ether, alcohol, and sulphurous acid:

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethylhydrogen}\\\text{sulphate.}}}{C_2H_5HSO_4} + \underset{\text{Water.}}{OH_2}$$

The product, when further heated, yields ethylene,—

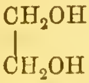
$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

If the ethylene be passed into bromine under water until all the bromine disappears, *ethylene dibromide*, $C_2H_4Br_2$, or *dibrom-ethane*, will be formed. For constitution, *see* page 468.

Properties.—A colourless and odourless gas, burning with a luminous flame.

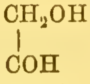
Ethylene Sulphate, $C_2H_4SO_4$, is said to be contained in the *Spiritus Ætheris Compositus*, B.P., a solution of 3 volumes of *heavy oil of wine* in 64 of ether and 128 of rectified spirit. The so-called "heavy oil of wine" is obtained by digesting spirit of wine and sulphuric acid together, then distilling, removing any acid from the distillate by washing with lime-water, and exposing the ethereal fluid to the air to facilitate escape of the more volatile fluids. The product is a mixture consisting probably of ethylene sulphate, ethyl sulphate, ether, dissolved ethylene, and other bodies.

Glycols.—The olefines form corresponding dihydric alcohols or glycols (named from glycol, the first member of the series), and these give two sets of aldehydes and acids. (See also p. 543.) Thus,—



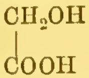
$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol.



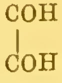
$$\begin{array}{c} CH_2OH \\ | \\ COH \end{array}$$

Glycollic aldehyde.



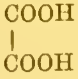
$$\begin{array}{c} CH_2OH \\ | \\ COOH \end{array}$$

Hydroxyacetic acid, or glycollic acid.



$$\begin{array}{c} COH \\ | \\ COH \end{array}$$

Glyoxal or Oxalic aldehyde.



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

Oxalic acid.

TABLE SHOWING RELATIONS BETWEEN PARAFFINS, OLEFINES, AND ACETYLENES.

	Paraffins, $C\ H_{2n+2}$.	Olefines, C_nH_{2n}.	Acetylenes, C_nH_{2n-2}.
Hydrocarbon	Ethane, C_2H_6, or $CH_3{\cdot}CH_3$	Ethylene, C_2H_4	Acetylene, C_2H_2
Alkyl Salts Chloro-derivatives . .	Ethyl Chloride, or Monochlorethane, C_2H_5Cl	Ethylene Chloride, or Dichlorethane, $C_2H_4Cl_2$	Acetylene Chloride, or Tetrachlorethane, $C_2H_2Cl_4$
Alcohol . .	Ethylic Alcohol, C_2H_5OH, or CH_3CH_2OH	Ethylene Glycol, $C_2H_4(OH)_2$, or $(CH_2OH)_2$	
Acid . . .	Acetic Acid, $CH_3{\cdot}CO{\cdot}OH$	Oxalic Acid, $(COOH)_2$	
Cyanide . .	Cyanethane, CH_3CH_2CN	Ethylene Cyanide, or Dicyanethane, $C_2H_4(CN)_2$	

RELATION OF PARAFFINS TO OLEFINES.

1st. The paraffins may be converted into olefines either by acting on alcohols of the paraffin series by sulphuric acid, or by acting on a monochloro-paraffin by caustic potash.

$$C_2H_5Cl + KHO = C_2H_4 + KCl + H_2O.$$

Monochlorethane. Ethylene.

Inversely, the olefines may be converted into paraffins. By combining an olefine with hydrochloric acid a monochloro-paraffin results, which, when acted on by nascent hydrogen, yields a paraffin.

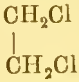
$$C_2H_4 + HCl = C_2H_5Cl$$

Ethylene. Monochlorethane.

$$2C_2H_5Cl + 2H_2 = 2C_2H_6 + 2HCl$$

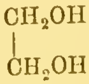
Monochlorethane. Ethane.

2nd. The bromine, chlorine, and iodine additive derivatives of the olefines, are either identical or isomeric with the substitution derivatives of the paraffins. Thus $C_2H_4Cl_2$ is either dichlorethane or ethylene chloride ; and the additive derivatives with the acids, such as hydrochloric, produce monosubstitution derivatives of the paraffins. In the case of the chloride, however, $C_2H_4Cl_2$, it has a different boiling point and specific gravity, according as it is prepared from ethylene and chlorine (*chloride of ethylene*, alpha-dichlorethane, or the old "Dutch liquid"), or from monochlorethane (chloride of ethyl) and chlorine (chloride of monochlorethyl, beta-dichlorethane, or *chloride of ethylidene*). The former may be represented by the formula $CH_2Cl \cdot CH_2Cl$, and the latter as $CH_3 \cdot CHCl_2$. It is the former also which yields glycol (by reaction of the chloride with silver acetate, and of the resulting ethylene acetate with an alkaline hydrate), hence the formula of the glycol also must be $CH_2OH \cdot CH_2OH$, and not $CH_3 \cdot CH(OH)_2$:—



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Chloride of ethylene.
(Dutch liquid.)



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

Hydrate of ethylene.
(Glycol.)

THE ACETYLENE SERIES OF HYDROCARBONS.

The members of the acetylene series, C_nH_{2n-2}, are characterized by forming metallic derivatives. *Acetylene* itself, C_2H_2, is formed during the passage of electric sparks between carbon points in an atmosphere of hydrogen; it is the only member which can be formed directly from its elements. Other members of the series are *Allylene*, C_3H_4; *Crotonylene*, C_4H_6; etc. The hydroxyl derivative of allylene, known as *propargyl alcohol*, has the formula C_3H_3OH.

Preparation.—Acetylene may be obtained by heating ethylene bromide (dibromethane) with caustic potash, and passing the gas into a well-cooled ammoniacal solution of cuprous chloride, with which it reacts, forming a red precipitate, probably having the formula $C_2H_2Cu_2O$ (Blochmann), called cuprous acetylide. The pure acetylene gas may be obtained from the copper compound by heating with hydrochloric acid. Acetylene is yielded in a steady stream when water is dropped on to carbide of barium. Acetylene is also formed by the incomplete combustion of coal gas, as when an air-gas burner is lighted below. It has an unpleasant odour, well known in every chemical laboratory in which air-gas lamps are used.

QUESTIONS AND EXERCISES.

What are the properties of ethylene, and how is it prepared?—What alcohols are derived from the olefine series?—Mention the relations between the paraffins and olefines.—Give three methods of preparing acetylene.

THE TERPENE SERIES OF HYDROCARBONS.

The terpene series have the general formula, C_nH_{2n-4}. *Valylene*, C_5H_6, is the lowest, and *terebenthene* or *pinene* $C_{10}H_{16}$, (pure oil of turpentine), the most common member of the series.

The hydrocarbons, called terpenes, $C_{10}H_{16}$, are very commonly met with in analysing the volatile oils. Very few of these oils have been artificially produced. Their fragrance appears to be due to the non-terpenoid constituent (Wallach). They differ from one another in the power of deviating a ray of polarized light to the right or left. They may be divided into classes, of which several are interesting in pharmacy: (*a*) *Terpenes* or *pinenes*, boiling at about 156° C., and found in ordinary turpentine and other oils; (*b*) *sylvestrene*, found in Russian and Swedish turpentine; (*c*) *phellandrene*, lævorotatory from *phellandrium aquaticum*, and dextrorotatory from eucalyptus oil (page 498), boiling point 170° C.; (*d*) *citrenes* (*limonenes*), boiling at about 175° C., and derived from the different species of citrus; (*e*) *di-pentene*, found in some turpentines and oils of camphor and elemi; (*f*) *terpinene*, occurring in oil of cardamoms. *Camphene*, *fenchene* and *terpinolene* are terpenes, but do not occur naturally in oils. The *sesquiterpenes* have the formula $C_{15}H_{24}$ and include cadinene, found in oils of cubebs, savin, cade, betel, camphor, galbanum, patchouli, juniper, asafœtida, colo, and olibanum; *caryophyllene*, found in oil of cloves, and other isomers of these. They boil at a much higher temperature than the terpenes, but resemble them in other respects.

Oil of *Turpentine* (*Oleum Terebinthinæ*, B.P.). Turpentine itself is really an oleo-resin of about the consistence of fresh honey. It flows naturally or by incision from the wood of most coniferous trees; larch (*Pinus Larix*) yielding *Venice turpentine*, *Abies balsamea* furnishing *Canadian Turpentine* or *Canada Balsam* (*Terebinthina Canadensis*, B.P.), the *bark* of *Pistachia terebinthus*, the variety termed *Chian Turpentine* (containing about 1 part of essential oil to 7 of resin), and the *Pinus australis* (*palustris*), *P. abies*, *P. pinaster* and *P. tæda*, affording the common American Turpentine. *Pinus maritima* gives the French or Bordeaux Turpentine, and *P. picea* the old fragrant Strasburg Turpentine. By distillation with steam, this crude turpentine is separated into colophony, *rosin*, or *resin*, which remains in the still, and *essential oil of turpentine*, often termed simply *turpentine*, *spirit of turpentine*, or "*turps*," which distils over. Mixed with alkali to saturate rosinous acids, and redistilled in a current of steam, oil of turpentine furnishes about 80 per cent. of *rectified oil of turpentine*. *Pinus sylvestris* and *P. Ledebourii* furnish Russian turpentine, which, according to Tildon, consists of two terpenes and cymene; and also (Wallach) a lævogyre limonene. This turpentine is probably a by-product in the preparation of common *wood tar* (*Pix Liquida*, B.P.); its odour is very pleasant, quite different from that of ordinary turpentine. The leaves of the *Pinus sylvestris*, or Scotch fir, are in

Germany broken down to a woolly condition, producing Pine Wool or Fir Wool, or wadding used in making vermin-repelling blankets; and this substance, or, still better, the fresh leaf, by distillation with water, yields *Fir-Wool Oil* (*Oleum Pini Sylvestris*, B.P.), consisting, according to Tilden, of two terpenes, like those of Russian turpentine, and cymene. This oil, diffused through water by aid of magnesia, forms the *Vapor Olei Pini Sylvestris*, B.P. The terpene of Bordeaux turpentine (terebenthene) rotates a ray of polarized light more than, and in the opposite direction to, the terpene of American turpentine.

Turpentine "commences to boil at about 320° F. (160° C.) and almost entirely distils below 356° F. (180° C.), little or no residue remaining," whereas petroleum spirit, with which turpentine might be mixed, covers much wider limits of temperature during its distillation. Petroleum spirit also, when the small round flame of the end of a piece of twine is brought near to some of the spirit in a cup, gives a momentary flash of flame at a much lower temperature than that at which turpentine flashes. Thus tested in the specially arranged flashing apparatus of the Petroleum Act, Mr. Boverton Redwood found that the flashing point of turpentine was lowered 10 degrees, Fahrenheit, by 1 per cent. of petroleum spirit. The specific gravity of oil of turpentine is from about 0·855 to 0·870.

Under the influence of heat and sulphuric acid or other chemical agents, pure oil of turpentine ($C_{10}H_{16}$) yields many derivatives of considerable chemical interest. Amongst them are two optically inactive terpene isomers named *terebene* and *colophene*, used for inhalation and as disinfectants and deodorizers. When acted on by gaseous hydrochloric acid, the product is a white crystalline monohydrochloride, $C_{10}H_{16}HCl$. Bromine acts violently on turpentine and terpenes, resulting in dibromides which yield cymene when heated, $C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr$. Crystals of *terpin hydrate*, $C_{10}H_{18}(OH)_2,H_2O$, also *terpinol*, $(C_{10}H_{16})_2,H_2O$, are used therapeutically instead of terebene.

Volatile Oils.

The *Volatile* or *Essential Oils* oxist in various parts of plants. They usually are mixtures of the liquid hydrocarbons or *elæoptens* (from ἔλαιον, *elaion*, oil, and ὂπτομαι, *optomai*, to see) with oxidized hydrocarbons, which are commonly solid or camphor-like bodies termed *stearoptens* (from *στέαρ*, *stear*, suet), and which on cooling often crystallize out; or on distilling an oil the stearopten may remain in the retort, being less volatile than the elæopten. The oils are also often associated with further oxidized bodies termed *resins*.

The process by which volatile oils are usually obtained from herbs, flowers, fruits, or seeds, may be imitated on the small scale by placing the material (bruised cloves or caraways, for instance) in a tubulated retort, adapting the retort to a Liebig's condenser, and passing steam, from a Florence flask, through a glass tube to the bottom of the warmed retort. The steam in its passage through the substance will carry the particles of oil over the neck of the retort into the condenser, and thence, liquefied and cooled, into the receiving vessel, where the oil will be found floating on the water. It may be collected by running off the distillate through a glass funnel having a stopcock in the neck, or by letting the water from the condenser drop into an old test-tube which has a small hole in the bottom, or any similar tube placed in a larger vessel, the water and oil being subsequently run off separately from the tube as from a pipette. The water will in most cases be the ordinary official medicated water of the material operated on (*Aqua Anethi*, *Anisi*, *Aurantii Floris*, *Carui*, *Cinnamomi*, *Fœniculi*, *Menthæ Piperitæ*, *Menthæ Viridis*, *Pimentæ*, *Rosæ*,—from *Rosæ Centifoliæ Petala*, B.P.,—*Sambuci*). Volatile oils, like fixed oils, stain paper; but the stain of the former is not permanent like that of the latter. Oils of lemon and orange are sometimes obtained by mere pressure of the rind of the fruit.

The presence of alcohol in an essential oil may be detected and its quantity estimated by shaking with an equal bulk of pure glycerine. The latter dissolves the alcohol, and is augmented in volume according to the amount of alcohol present (Boettger). (For tests for alcohol, *see* Index, "Alcohol.")

A large number of volatile oils are employed in medicine, either in the pure state, in the form of saturated aqueous solution (medicated waters), solution in spirit of wine, 1 in 5 (*Essentia Anisi* and *Essentia Menthæ Piperitæ*, B.P.) and 1 in 50 (*Spiritus Cajuputi*, *Cinnamomi*, *Juniperi*, *Lavandulæ*, *Menthæ Piperitæ*, *Myristicæ*, *Rosmarini*), or as leading constituents in various barks, roots, leaves, etc. *Perfumes* ("scents" or "essences," including "lavender-water" and "eau de Cologne") are for the most part solutions of essential oils in spirit of wine, or spirituous infusions of materials containing essential oils. The following oils are, directly or indirectly, official in the Pharmacopœias*:—1. Volatile oil of *Bitter Almond* (*vide* Index). 2. Oil of the fruits of *Ajwain* or *Omum*, *Carum Ajowan*, or *Ptychotis Ajowan* (*Fructus Ptychotis*, P.I.), contains *cymol* or *cymene* ($C_{10}H_{14}$), and a stearopten (*Ajwainka-phul*, flowers of ajwain) identical with *thymol*, $C_{10}H_{14}O$. 3. Oil of *Dill* (*Oleum Anethi*, B.P.), a pale, yellow, pungent, acrid liquid distilled from dill-fruit; it contains a hydrocarbon, *anethene* ($C_{10}H_{16}$), and an oxidized oil ($C_{10}H_{14}O$) identical with the carvol of oil of caraway (Gladstone). 4. Oil of *Aniseed* (*Oleum Anisi*, B.P.), a colourless or pale yellow liquid, of sweetish warm flavour, distilled in Europe from the anise fruit (*Pimpinella Anisum*), but chiefly, in China, from the fruit of star-anise (*Illicium Anisatum*); it is a mixture of a hydrocarbon isomeric with oil of turpentine and *anethol*, a stearopten ($C_{10}H_{12}O$) which crystallizes out at low temperatures. The melting point of anethol is between 74° and 75° F. (Flückiger). The congealing point of the natural oils appears to be dependent on the proportion of the fluid to the solid constituent, a very small quantity of the former lowering the congealing and melting points very considerably. 5. Oil of *Chamomile* (*Oleum Anthemidis*, B.P.), a bluish or, when old, yellow oil, of characteristic odour and taste, distilled from chamomile-flowers (*Anthemidis Flores*, B.P.). The official variety (*Anthemis nobilis*) yields about 0·2 per cent. of an oil composed of a hydrocarbon ($C_{10}H_{16}$) and an oxidized portion ($C_{10}H_{16}O_2$) which, heated with potash, gives *angelate of potassium* ($KC_5H_7O_2$), whence is obtained *angelic acid* ($HC_5H_7O_2$). According to Demarçay, Kopp, and Köbig, the oil is a mixture of the angelates of butyl and amyl and similar bodies. Naudin has also obtained from chamomiles *anthemen*, a hydrocarbon crystallizing in needles. The flowers of another variety (*Matricaria Chamomilla*) contain a stearopten ($C_{10}H_{16}O$) having the composition of laurel-camphor. 6. Oil of *Horse-radish* root (*Armoraciæ Radix*, B.P.) is, according to Hofmann, the sulphocyanate of butyl or tetryl (C_4H_9CNS): it is the chief active ingredient of *Spiritus Armoraciæ Compositus*, B.P. 7. Oil of *Bitter-Orange* rind (*Aurantii Cortex*, B.P., *Aurantii Fructus*, B.P.), the flavouring constituent of the official syrup of the *peel* (*Syrupus Aurantii*, B.P.), and the oils of various species of *Citrus*; namely:—8. *Lemon* (*Oleum Limonis*, B.P., from *Limonis Cortex*, B.P.); 9. *Lime*; 10. *Bergamot*; 11. *Citron* and a variety of citron termed *cedra*, resemble each other in composition, all containing *hesperidene*, a hydrocarbon ($C_{15}H_{34}$), and a small quantity of oxidized hydrocarbons [$C_{10}H_{10}O_5$, $C_{15}H_{16}O$, and (Wright and Piesse) $C_{20}H_{30}O_3$], etc. Tilden states that lemon oil distilled from the fresh peel consists chiefly of a terpene, $C_{10}H_{16}$, boiling at 176° C., with small quantities of a terpene boiling below 160°, and a hydrous terpene, the odour of the oil being due to the mixture. Oil of bergamot appears to owe its fragrance to 40 or 50 per cent. of *linalool acetate*, $C_{10}H_{17}C_2H_3O_2$. It also contains a stearopten, *bercapten*, $C_{12}H_8O_4$. Expressed lime essence contains a soft resin. 12. Oil of *Neroli*, or *Orange-Flower*, the aqueous solution of which is official in the forms of water (*Aqua Aurantii Floris*, B.P.) and syrup (*Syrupus Aurantii Floris*, B.P.), contains a fragrant hydrocarbon ($C_{10}H_{16}$), colourless when fresh, but becoming red on exposure to light, and an inodorous, oxidized hydrocarbon. Strong acids, especially nitric, attack the oil in orange-flower water, colouring the fluid of a rose tint. 13. Oil of *Petit Grain*, distilled from the leaves and shoots of the orange-tree, consists chiefly of *aurantiol acetate*, $C_{10}H_{17}C_2H_3O_2$. 14. The leaves of *Boldo* (*Peumus Boldus*), a Chilian shrub (tonic and hepatic), yield two per cent. of essential oil (and, according to Bourgon and Verne, an alkaloid, *boldine*). 15. Oil of *Buchu-leaves* (*Buchu Folia*, B.P.) consists chiefly of a fluid oil, $C_{10}H_{18}O$, holding in solution a crystalline stearopten, diosphenol, ($C_{14}H_{22}O_3$, Flückiger; $C_{10}H_{16}O_2$, Spica, Shimoyana also). 16. Oil of *Cannabis indica*, *see* page 505. 17. Oil of (the lesser) *Cardamoms*, from the seeds of the capsules (*Cardamomi Semina*, B.P.), is chiefly a hydrocarbon ($C_{10}H_{16}$) isomeric with oil of turpentine (terpilene and probably limonene) and a camphor resembling turpentine-camphor

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* The student is not expected to remember, but to understand, all that follows respecting the volatile oils.

$(C_{10}H_{16}3H_2O)$. 18. Oil of *Cajuput* (*Oleum Cajuputi*, B.P.) is a mobile bluish liquid, consisting of *hydrous cajuputene* or *cajuputol* ($C_{10}H_{16}$, H_2O); *cajuputene*, $C_{10}H_{16}$; *cineol*, $C_{10}H_{17}OH$; a sesquiterpene, $C_{15}H_{24}$; as well as butyric, valeric and benzoic aldehydes. The latter, repeatedly distilled from phosphoric anhydride, yields cajuputene itself ($C_{10}H_{16}$), which has the odour of hyacinths. Fresh cajuput-oil has a green hue, which is perhaps transient, for the colour of the oil of trade is due to copper (Guibourt and Histed): certainly the green colouring-matter of pure cajuput-oil is organic and either oily or chlorophylloid. 19. Oil of *Caraway*-fruit (*Oleum Carui*, B.P., from *Carui Fructus*, B.P.) is a mixture of *carvene* ($C_{15}H_{24}$) and *carvol* ($C_{10}H_{14}O$). 20. Oil of *Cloves* (*Oleum Caryophylli*, B.P.) and of *Pimento* (*Oleum Pimentæ*, B.P.), both heavier than water, contain a liquid hydrocarbon ($C_{15}H_{24}$), *eugenol* ($C_{10}H_{12}O_2$), a solid body, *eugenin*, isomeric with the eugenic acid, a second crystalline substance, *caryophyllin* ($C_{10}H_{16}O$), isomeric with common camphor, and a salicylic compound. 21. Oil of *Cascarilla*-bark (*Cascarillæ Cortex*, B.P.) has not been fully examined. 22. Oil of *Cinnamon*-bark (*Cinnamomi Cortex*, B.P.) and of *Cassia*-bark is mostly cinnamic aldehyde (C_8H_7COH). Boiled with nitric acid, it furnishes benzoic aldehyde (C_6H_5COH) and benzoic acid (C_6H_5COOH), with chloride of lime it yields benzoate of calcium $(C_6H_5COO)_2Ca$, and with caustic potash gives cinnamate of potassium (C_8H_7COOK). The specific gravity of oil of cinnamon (*Oleum Cinnamomi*, B.P.) varies from 1·025 to 1·050. 23. Oil of *Citronella*, a *Grass Oil*, from *Andropogon nardus*, is chiefly composed of *citronellol* ($C_{10}H_{16}O$ and $C_{10}H_{18}O$, Wright), probably isomeric with the *absinthol* of wormwood (Gladstone). Kremer also obtains heptoic aldehyde ($C_7H_{14}O$), a terpene ($C_{10}H_{16}$), etc. 24. Oil of *Copaiva* (*Oleum Copaibæ*, B.P.) and, 25, of *Cubebs* (*Oleum Cubebæ*, B.P.) are hydrocarbons having the formula $C_{15}H_{24}$. This *cubebene* is sometimes associated with a camphor, *hydrous cubebene* ($C_{15}H_{24}$, H_2O). Oil of cubebs also contains a small quantity of a terpene ($C_{10}H_{16}$). 26. Oil of *Coriander* (*Oleum Coriandri*, B.P.) seems to have the composition of hydrous oil of turpentine ($C_{10}H_{16}$, H_2O). 27. The fruits of *Cumin*, or *Cummin* (*Cuminum Cyminum*), an ingredient of many curry-powders, contain about 3 per cent., and those of *Water Hemlock* or *Cowbane* (*Cicuta virosa*) about 1¼ per cent. of an essential oil composed of *cymol* or *cymene* ($C_{10}H_{14}$), and *cumic* *aldehyde* ($C_9H_{11}COH$). The latter is an aldehyde readily uniting with alkaline bisulphites and by oxidation yielding *cuminic acid* ($C_9H_{11}COOH$). Cymol also occurs in *Garden Thyme* (*Thymus vulgaris*). 28. *Eucalyptus globulus* furnishes *eucalyptol* (*Oleum Eucalypti*, B.P.), an oil the more volatile and chief portion of which is *cymene* and a *terpene* ($C_{10}H_{14}$ + $2C_{10}H_{16}$, *phellandrene*, p. 492, more readily alterable than other terpenes), together with an oxidized portion, $C_{10}H_{14}O$ and $C_{10}H_{16}O$, and an oil having the same composition as *cajuputol* and as the chief constituent of *wormseed oil*, $C_{10}H_{18}O$ or $C_{10}H_{16}$, H_2O. Different species of eucalyptus may yield oils differing in specific gravity, flavour and odour. *E. maculata*, *var. citriodora*, contains an aldehyde, or ketone, similar to that of citronella. Like the turpentines the eucalyptus oils are good solvents of resins. Voiry states that eucalyptol is present also in the oil of *Lavandula spica*, oil of *spike* or "foreign" oil of lavender. *Red gum* (*Eucalypti Gummi*, B.P.) is from the bark of *E. rostrata* and other species, and is used solely for its astringent properties. 29. *Elecampane*-root (*Inula Helenium*) by distillation with water yields solid volatile *helenin* (C_6H_8O), a camphor-oil or *inulol* ($C_{10}H_{16}O$), and *inulic anhydride* or *lactone* ($C_{15}H_{20}O_2$), as well as, according to Marpmann, crystals of *alantic acid* ($C_{15}H_{22}O_3$) and fluid *alantol* ($C_{20}H_{32}O$) each more powerfully antiseptic than helenin. 30. Oil of *Fennel*-fruit (*Fœniculi Fructus*, B.P.) differs in odour, but contains the same proximate constituents as oil of anise. 31. Oil of *Geranium*, or *Ginger Grass* oil, from *Andropogon schœnanthus*, and various species of *Pelargonium*, contains *geraniol* ($C_{10}H_{18}O$). 32. *Grains of Paradise* (*Amomum melegueta*), Guinea Grains or Melegueta Pepper, *Semina Cardamomi Majoris*, contain essential oil ($C_{10}H_{16}$ and $C_{10}H_{16}O$) and a highly pungent principle, termed by Thresh *paradol*, $C_9H_{14}O_2$, isomeric with the capsaicin of the same chemist. 32*a*. Oil of *American Pennyroyal* (*Hedeoma*, U.S.P., "the leaves and tops of *Hedeoma pulegioides*" contains *hedeomol* ($C_{10}H_{18}O$), and yields *isoheptoic* acid ($C_7H_{14}O_2$), and other substances (Kremer). 33. Oil of *Juniper* (*Oleum Juniperi*, B.P.) contains a hydrocarbon ($C_{10}H_{16}$) which by contact with water yields a white crystalline hydrous compound ($C_{10}H_{16}$, H_2O) and a polymeric hydrocarbon ($C_{20}H_{32}$). 34. Oil of *Lavender* (*Oleum Lavandulæ*, B.P.) has not been satisfactorily examined. 35. Oil or butter or camphor of *Orris* (*Iris Florentina*) is a soft solid lighter than water.

Flückiger and Hanbury found it to be chiefly myristic acid associated with a little essential oil. 36. Oil of *Peppermint* (*Oleum Menthæ Piperitæ*, B.P.) consists of a hydrocarbon, *menthene* ($C_{10}H_{18}$), different from that of most volatile oils, depositing crystalline peppermint camphor known as menthol, $C_{10}H_{18}$, H_2O, when exposed to low temperatures. It is official (*Menthol*, B.P., also *Emplastrum Menthol*, B.P.), and has the following characters : "In colourless acicular crystals, usually more or less moist from adhering oil ; or in fused crystalline masses. Its melting-point should not exceed 110° F. (43·3° C.) It has the odour and flavour of peppermint, producing warmth on the tongue, or, if air be inhaled, a sensation of coolness. It is sparingly soluble in water, and readily soluble in rectified spirit, the solutions having a neutral reaction. Boiled with sulphuric acid diluted with half its volume of water, menthol acquires an indigo-blue or ultramarine colour, the acid becoming brown. It should be entirely dissipated by the heat of a water-bath." It is also yielded by the oil of *Mentha arvenis* (*vars. piperascens* and *glabrata*). 37. Oil of *Spearmint* (*Oleum Menthæ Viridis*, B.P.), the Common Mint of the kitchen garden, contains a liquid having the formula $C_{10}H_{20}O$ or $C_{10}H_{18}H_2O$, also, according to Gladstone, an oil ($C_{10}H_{14}O$), isomeric with carvol. 38. Oil of *Pennyroyal* (*Mentha Pulegium*) contains, according to Kane, $C_{10}H_{16}O$ (*pulezone* ; Plaisner). 39. Oil of *Nutmeg* (*Oleum Myristicæ*, B.P.) is composed of a hydrocarbon, *myristicene* ($C_{10}H_{16}$), and *myristicol* ($C_{10}H_{16}O$), and cymene ($C_{10}H_{14}$) (Gladstone). *Mace*, the arillus or net-like envelope of the nutmeg, appears to yield similar bodies and also *myristicin*, $C_{12}H_{14}O_3$ (Semmler). 40. Oil or *Otto* or *Attar* of *Cabbage-Rose petals* (*Rosæ Centifoliæ Petala*, B.P.) gives the fragrance to rose-water (*Aqua Rosæ*, B.P.). It resembles most other volatile oils in being composed of a hydrocarbon and an oxidized portion, but differs from all in this respect, that the hydrocarbon is solid and is destitute of odour, while the oxygenated constituent is liquid and the source of the perfume. According to Flückiger, the solid hydrocarbon ($C_{18}H_{16}$) yields succinic acid as the chief product of its oxidation by nitric acid, and in other respects affords evidence of belonging to the paraffin series of fats. 41. Oil of *Rosemary-tops* (*Oleum Rosmarini*, B.P.) exists in the plant to the extent of from 1½ to 3 parts per 1,000. It chiefly consists of a hydrocarbon ($C_{10}H_{16}$) resembling that from Myrtle, *Myrtus communis*, but also contains camphor ($C_{10}H_{16}O$) and borneol ($C_{10}H_{18}O$) in variable proportions. 42. Oil of *Rue* (*Oleum Rutæ*, B.P.) contains a small quantity of hydrocarbon ($C_{10}H_{16}$) with some rutic aldehyde ($C_{10}H_{20}O$), and methyl-nonyl ketone, $C_{11}H_{22}O$ or $CH_3—CO—C_9H_{19}$. Gorup-Besanez and Grimm have obtained oil of rue ($C_{11}H_{22}O$) artificially, as one of the products of the destructive distillation of acetate and caprate of calcium (*see* Ketones). According to Greville Williams, it is chiefly euodic aldehyde ($C_{11}H_{22}O$), some lauric aldehyde ($C_{12}H_{24}O$) also being present. 43. Oil of *Sage* contains about 40 per cent. of salviol, $C_{10}H_{16}O$; about 20 per cent. of two $C_{10}H_{16}$ hydrocarbons boiling at 156° and 167° C. respectively; about 10 per cent. of a camphor, $C_{10}H_{16}O$; and about 10 per cent. of cedrene, $C_{15}H_{24}$ (Muir). 44. Oil of *Savin* (*Oleum Sabinæ*, B.P.) obtained from the tops (*Sabinæ Cacumina*, B.P.) of *Juniperus Sabina* contains several hydrocarbons, but none isomeric with oil of turpentine (Tilden). 45. Oil of *Elder-flowers* (*Sambuci flores*, B.P.) occurs in very small quantity; it has a butyraceous consistence; it contains a hydrocarbon, *sambucene* ($C_{10}H_{16}$), and probably a camphor. 46. Oil of *Sandal-wood* (*Oleum Santali*, B.P.) is composed (Chapoteaut) of two bodies: mostly of a substance having the formula $C_{15}H_{24}O$ (boiling at 572° F.), and a small quantity of a substance having the formula $C_{15}H_{26}O$ (boiling at 600° F). It occurs to the extent of about 1 per cent. in the fragrant white or yellow sandal-wood of India, *Santalum album*, a small tree of the natural order Santalaceæ, and not to be confounded with the *Pterocarpus santalinus*, a tree of the natural order Leguminosæ, and furnishing the inodorous Red Sandal-wood or Red Sander's Wood or *Barwood* of the dyer. 47. Oil of *Sassafras-root*, sp. gr. 1·094 (*Sassafras Radix*, B.P.) contains nine-tenths of its weight of *Safrol* or *Sassafrol*, $C_{10}H_{10}O_2$, also *eugenol* and a small quantity of a terpene. Sassafras camphor, $C_{10}H_{10}O_2$, is deposited when the oil is exposed to a low temperature. 48. Oil of *Mustard* (*Oleum Sinapis*, B.P.) is sulphocyanate of allyl (*see* Index). If contaminated with alcohol, its sp. gr. is below 1·015. 49. Oil of *Sweet Flag* (*Acorus calamus*) contains the hydrocarbon $C_{10}H_{16}$. (The rhizome also contains *Acorin*, $C_{36}H_{60}O_6$, a bitter glucoside and an alkaloid, *calamine*.) 50. Oil of common garden *Thyme* (*Thymus vulgaris*) is composed of *cymene* or *cymol* ($C_{10}H_{14}$), *thymene* ($C_{10}H_{16}$), and *thymol* ($C_{10}H_{14}O$).

Thymol crystallizes out when oil of thyme or of ptychotis, etc., is kept at a low temperature for a day or two. It may also be obtained by shaking the oils with caustic alkali, and treating the separated alkaline liquid with an acid. It may be purified by distillation or by crystallization from alcohol. It would seem that as an antiseptic thymol is far stronger than carbolic acid. 51. Oil of *Turmeric* (*Curcuma longa*) is said by Jackson and Menke to be chiefly an alcohol having the formula $C_{19}H_{27}OH$. They name it *turmerol.* It is a light yellow volatile oil, having the sp. gr. 0·902. It is to this oil that turmeric (hence curry powder, partly) owes its flavour and odour. 52. Oil of *Valerian-root* (*Valerianæ Rhizoma*, B.P.) is a mixture of a hydrocarbon, *valerene* or *borneene* ($C_{10}H_{16}$), *valerol* ($C_6H_{10}O$), and (Gersek) 10 per cent. of borneol valerianate. Valerol slowly oxidizes to valerianic acid, known by its smell. A similar change occurs at once if oil of valerian be allowed to fall, drop by drop, on heated caustic potash : $C_6H_{10}O + 3KHO + H_2O = K_2CO_3 + C_4H_9COOK + 3H_2$. By the action of sulphuric acid on the valerianate of potassium thus produced, valerianic acid is obtained. 53. Oil of *Verbena*, *Lemon-grass* Oil, or *Indian Melissa* Oil, is obtained from *Andropogon citratus* (*Oleum Andropogi Citrati*, P.I.). 54. Oil of *Ginger* (*Zingiber*, B.P.), is, according to Thresh, a complex mixture of hydrocarbons and their oxidation products; cymene ($C_{10}H_{14}$) is present, a terpene, aldehydes, and ethereal salts. (For an analysis of ginger, by Thresh, and for papers on " Soluble Essence of Ginger," *see* the *Pharmaceutical Journals* for August 30 and September 6, 1879, and March 4, 1882.)

Caoutchouc or *India-rubber*, and *Gutta Percha.*

Caoutchouc is the hardened juice of *Dichopsis Gutta*, *Hevea* (*Siphonia*) *Brasiliensis*, *Castilloa elastica*, *Urceola elastica*, *Ficus elastica*, and other plants. Heated moderately with sulphur, it takes up 2 or 3 per cent., and forms *vulcanized india-rubber ;* at a higher temperature a hard horny product, termed *ebonite*, or *vulcanite*, results. *Gutta Percha* (*Gutta Percha*, B.P.) is the concrete drop or juice of the *percha* (Malay) tree, the *Isonandra gutta*, and of other Sapotaceous plants. White gutta percha is obtained by precipitating a solution of ordinary gutta percha in chloroform by alcohol, washing the precipitate with alcohol, and finally boiling in water and moulding into the desired form while still hot. The official solution of gutta percha (*Liquor Gutta Percha*, B.P.) is made by digesting *thin* slices of gutta percha in 12 parts by weight of chloroform, and then "fining" by shaking with 1 part of carbonate of lead and setting aside till the fluid is clear.

These two elastic substances, in the pure state, are hydrocarbons (xC_5H_4), usually slightly oxidized. When caoutchouc is distilled, a terpene, $C_{10}H_{16}$, called caoutchin, is obtained.

Camphors.

In addition to the stearoptens or camphors already mentioned as being contained in or formed from volatile oils, there is one that is a common article of trade. It is obtained from the wood of *Camphora officinarum*, or Camphor-laurel, in Japan (termed, in Europe, Dutch camphor, because imported by the Dutch) and in China (known as Formosa camphor), by a rough process of distillation with water, and is resublimed in this country (*Camphora*, B.P.). The formula of laurel-camphor is $C_{10}H_{16}O$. Sp. gr. 0·990 to 0·995; melting point, 175° C.; boiling point, 205° C. Bromine heated with camphor gives *monobrom-camphor* ($C_{10}H_{15}BrO$) and hydrobromic acid. Monobrom-camphor is camphor in each molecule of which an atom of hydrogen has been displaced by one of bromine. Recrystallized, it occurs in white prisms. The essential oil, from which doubtless camphor is derived by oxidation, is easily obtained from the wood, and is occasionally met with in commerce under the name of *liquid camphor* or *camphor-oil*. It contains hydrocarbons resembling terebinthene and citrene, and hydrous camphor ($C_{10}H_{16}O, H_2O$) as well as camphor. By exposure to air it becomes oxidized and deposits common camphor. Camphor distilled with phosphoric anhydride yields cymene, $C_{10}H_{14}$. There is another kind of camphor, *Borneol*, in European markets, less common than laurel-camphor, but highly esteemed by the Chinese; it is obtained from the *Dryobalanops aromatica*, and denominated Sumatra or Borneo camphor. It differs slightly from laurel-camphor in containing more hydrogen, its formula being $C_{10}H_{18}O$. It may be obtained by acting on camphor with hydrogen, the camphor being dissolved in some inert liquid such as toluene, and sodium added: the sodium forms a compound, $C_{10}H_{15}ONa$, while the hydrogen thus liberated acts on another portion of the camphor, forming borneol, $C_{10}H_{17}(OH)$—a better result being obtained if absolute alcohol is used instead of toluene (Jackson and Menke). It is accompanied in the tree by a volatile oil ($C_{10}H_{16}$) isomeric with oil of turpentine. This oil, *borneene*, is also occasionally met with in trade, under the name of *liquid camphor* or *camphor-oil*, but differs from laurel-camphor oil in not depositing crystals on exposure to air.

The constitution of the camphors is still somewhat doubtful. Camphor is soluble to a slight extent in water (40 grains per gallon, Pooley). The official Camphor Water (*Aqua Camphoræ*, B.P.), or *camphor mixture*, is such a solution.

Common camphor, and many other of the camphors, oily hydrocarbons, and oxidized hydrocarbons, yield *camphoric acid*, $C_8H_{14}(COOH_2)$, and camphoronic acid, $C_7H_9(OH)(COOH)_2$, when attacked by oxidizing agents. Such reactions indicate natural relationships. Camphoric acid is a good antiseptic.

Cantharidin ($C_{10}H_{12}O_4$), the active blistering principle of cantharides (*Cantharis*, B.P.) and other vesicating insects (such as *Mylabris cichorii* or *Telini Fly*, P.I., common in India), has most of the properties of a camphor or a stearopten. It slowly crystallizes, from an alcoholic tincture of the beetles, in fusible, volatile, micaceous plates. The following process for the extraction of cantharidin is by Fumouze: Powdered cantharides are macerated with chloroform for twenty-four hours; and this treatment is repeated twice with fresh quantities of solvent, the residue having been well squeezed each time. The collected solutions are then distilled, and the dark-green residue treated with bisulphide of carbon, which dissolves fatty, resinous, and other matters, and precipitates the cantharidin. The precipitate is placed on a filter, washed with bisulphide of carbon, and recrystallized from chloroform. The same process, omitting the final recrystallization, may be used for the quantitative estimation of cantharidin in cantharides. The average quantity found is from four to five, or occasionally ten or even twelve, parts in one thousand. Cantharidin is readily soluble in warm glacial acetic acid (Tichborne), and still more readily in acetic ether, or chloroform. Cantharides from which the fat has been removed by petroleum ether yield their cantharidin with great facility.

Massing and Dragendorff consider cantharidin to be an anhydride, and that with the elements of water it forms *cantharidic acid* ($H_2C_{10}H_{12}O_5$). Piccard gives the vapour density of cantharidin as about 6·5, and its formula $C_{10}H_{12}O_4$. Homolka assigns to it the formula $C_8H_{13}O_2 \cdot CO \cdot COOH$.

Resins, Oleo-Resins, Gum-Resins.

Resins seem to be the oxidized products of terpenes and the allied hydrocarbons; they occur in plants, generally in association with volatile oils. They closely resemble camphors and stearoptens, but are not volatile, and differ from oils and fats mainly in being solid and brittle. For convenience they are classified as resins, oleo-resins, and gum-resins, the distinctions being founded as much on physical as on chemical properties.

Oleo-resins are mixtures of a resin and a volatile oil.

Gum-resins are mixtures of a resin or oleo-resin and gum.

Balsams are commonly described as resins or oleo-resins which yield benzoic and cinnamic acids; they are Benzoin (*Benzoinum*, B.P.), Balsam of Peru (*Balsamum Peruvianum*, B.P.), Balsam of Tolu (*Balsamum Tolutanum*), and Storax, and are treated of under the respective acids.

Some oleo-resins, containing neither of the above acids, are often termed balsams (*e.g.* balsam of copaiva, and Canada balsam); these will be treated under the head of Oleo-resins.

A physico-chemical method for the identification of the chief resins, gum-resins, and balsams will be found in the *Pharmaceutical Journal* for November 17th, 1877.

Resins appear to be somewhat antiseptic. Beer is said never to turn sour in casks lined with Burgundy pitch. The resin of hops has, perhaps, a similar effect in retarding oxidation of alcohol.

RESINS.*—1. *Resin*, *rosin*, or *colophony* (*Resina*, B.P.), is the type of this class. Its source is the oleo-resin or true turpentine of the conifers, a body which by distillation yields spirit of turpentine and a residuum of rosin. "Brown" and "white" rosin are met with in trade. The former is the residue of American, the latter of Bordeaux turpentine (from *Pinus Abies*, etc., and *Pinus maritima* respectively). The chief constituents of brown resin are *pinic acid* ($HC_{20}H_{29}O_2$) and *sylvic acid*, identical in composition, but differing in properties (*vide* Isomerism), the former being soluble and the latter insoluble in cold spirit of wine. White resin or "galipot" is chiefly *pimaric acid*, also isomeric with pinic acid. Pinic acid, cautiously heated, yields *colophonic* or *colopholic acid*. Rosin, by destructive distillation, yields *resin oil*, the first portion being "pale," the next "blue," and the third "green resin oil." Mixed with other oils, they are used for lubricating purposes and in the manufacture of printing ink. Among the products of the destructive distillation of rosin, Tichborne has found "*colophonic hydrate*" ($C_{10}H_{22}O_3$, H_2O), a white inodorous crystalline substance, and by depriving this of water has obtained white crystalline *colophonine* ($C_{10}H_{22}O_3$). Resin is soluble in oil of turpentine. Contact with sulphuric acid immediately colours it strongly red. It is a constituent of eight of the fourteen Plasters (*Emplastra*) of the British Pharmacopœia. 2. *Arnicin* ($C_{20}H_{30}O_4$), the chief acrid and one of the active principles of the rootlets and rhizome of Arnica (*Arnicæ Rhizoma*, B.P.), is a resin, and, probably, a glucoside. 3. *Cannabin*, said to be the active principle of *Indian Hemp* (*Cannabis Indica*, B.P.), was obtained in 1846 by T. and H. Smith, and is a resin. Personne in 1857 isolated a volatile oil, also said to possess much medicinal activity, consisting of *cannabene* ($C_{18}H_{20}$) and a solid crystalline "*hydride of cannabene*" ($C_{18}H_{22}$). A sesquiterpene ($C_{15}H_{24}$) is also said to be present. Preobraschensky has stated, and since re-asserted, that the active principle is nicotine. Kennedy searched for nicotine by two methods, but found none. Hay found an alkaloid, *tetano-cannabine;* Siebold and Bradbury, also H. F. Smith, an alkaloid termed *cannabinine*. Warden and Waddell, after careful investigations, consider that the active principle of the plant has yet to be isolated. Jahns finds choline present. The native names of Indian hemp, that is, of the cultivated "dried flowering or fruiting tops of the female plants of *Cannabis sativa*," are *ganga* and *gunjah*. It is chiefly grown in Bengal. *Guaza* is the name of the Bombay product which includes the wild plant. Both are used for smoking, and form the equivalent of the tobacco luxury of western nations. *Bhang*, or *sidee*, consists of the dried leaves, fruit, and twigs of the wild plant. Its infusion is drunk, as tea is in Europe and elsewhere. *Hashish*, made from bhang, corresponds to our *Extractum Cannabis Indicæ*, B.P. *Charas* or *churras* is a resinous exudation of the plant, and is also used for smoking. All these preparations are stimulating and narcotic. 4. *Capsicum-fruit* contains a resin (p. 508). 5. *Castorin*, a resinous matter, is the name given to the chief constituent of *Castor* (*Castoreum*, B.P.), the dried preputial follicles and included secretion of the Beaver (*Castor Fiber*). 6. *Copal.*—The best copal is the exuded resin of trees of extinct forests, and is found beneath the surface of the ground in the neighbourhood of existing trees. It appears to be a mixture of acids, but its character is still obscure. 6*a*. *Doundaké-bark*, an African febrifuge, from *Sarcocephalus esculentus*, owes its activity to resinoid substances, according to Heckel and Schlagdenhauffen. 7. *Dragon's Blood*, a crimson-red resin found as an exudation on the mature fruits of a Rotang or Rattan Palm (*Calamus draco*). It consists of resins having the probable formula $C_{20}H_{24}O_4$ and $C_{20}H_{20}O_4$ (Johnston). 8. *Ergotin* is a very active resinoid constituent of *Ergot* (*Ergota*, B.P.), or the sclerotium (compact mycelium or spawn) of *Claviceps purpurea*, produced within the pales and replacing the grain of the common rye, *Secale cereale*. According to Wenzell, ergot contains two alkaloids, *ecboline* and *ergotine*, to the former of which, he says, the activity of ergot is due. Blumberg considers these alkaloids to be identical. Tanret states that an unstable alkaloid termed *ergotinine* occurs in ergot to the extent of 1 per 1,000, and that it is accompanied by a camphor; also *ergosterin*, $C_{26}H_{40}$, OH_2O, resembling cholesterin. Dragendorff and Podwissotzki assert that ergot owes most of its activity to *sclerotic* or *sclerotinic acid*, present to the extent of about 4 per cent. Recent investigations seem to show that *cornutine* is an active alkaloid of ergot, associated with ergotinic and sphacelinic acids, picrosclerotine and ergotinine. The activity really seems to be due to a combination of alkaloids and acids, and not to any one constituent, as no principle representing the full activity of ergot has been extracted. Ergot also contains *choline*, which by decomposition may yield trimethylamine. "*Ergotin*" (*Ergotinum*, B.P.) is an alcoholic extract of an aqueous extract of ergot. 9. *Guaiacum-resin* is a mixture of substances (*see* Index). 10. *Jalap-resin* (see Index.) 11. *Kousso* (*Cusso*, B.P.) yields yellow crystals of a resinoid body readily soluble in alkaline liquids, *kosin* or *koussin* ($C_{31}H_{38}O_{10}$). It is, perhaps, an anhydride. 12. *Mastic* (*Mastiche*, B.P.) is a resinous exudation obtained by incision from the stem of the Mastic or Lentisk tree. Nearly nine-tenths of mastic is *mastichic acid*

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* The student is not expected to remember, but to understand, all that follows respecting the resins.

($C_{20}H_{32}O_3$), a resin soluble in alcohol; the remainder consists of *masticin* ($C_{20}H_{32}O$), a tenacious elastic resin and a terpene having the formula $C_{10}H_{16}$. 13. *Mezereon*, the dried bark (*Mezerei Cortex*, B.P.) of *Daphne Mezereum*, Mezereon, and *Daphne laureola*, Spurge Laurel, owes its acridity to a resin. 14. *Pepper* contains resin (*see* Index). 15. *Burgundy pitch* (*Pix Burgundica*, B.P.) is the melted and strained exudation from the stem of the Spruce Fir, *Abies excelsa*. The term Burgundy is a misnomer, the resin never having been collected at or near Burgundy—Finland, and to a smaller extent, Baden, and Austria being the countries whence it is derived. Its constituents closely resemble those of common resin. It is often adulterated and imitated by a mixture of resin with palm-oil, water, etc., from which it may be readily distinguished by its duller yellow colour, highly aromatic odour, greater solubility in alcohol, and almost complete solubility in twice its weight of glacial acetic acid (Hanbury). 16. *Podophyllum-resin.*—In preparing the resin of podophyllum or May-apple (*Podophylli Resina*, B.P.), an alcoholic extract of the rhizome and rootlets (*Podophylli Rhizoma*, B.P.) is poured into cold water; the resin is then deposited. This resin is the chief active principle of podophyllum-root. According to Guareschi, podophyllin contains a glucoside resembling convolvulin. Podwissotzki has extracted from podophyllum a little crystalline colouring matter, fat, a bitter crystalline acid, a bitter crystalline neutral principle, and an amorphous acid resin. Kürsten states that the latter yields a crystalline active substance, *podophyllotoxin*, $C_{23}H_{24}O_9$. 17. *Pyrethrin* is the name of the acrid resinous active principle of the root of *Anacylus pyrethrum* or *Pellitory-root* (*Pyrethri Radix*, B.P.). According to Buckheim, the action of alkalies breaks it up into piperidine and pyrethric acid. The crystalline poisonous principle obtained by Bellesme from *Pyrethrum carneum*, the powder of which (and *P. roseum*, and especially *P. cinerariæfolium*, or Dalmatian Insect Powder) is the well-known "insecticide," has not yet been analysed. 18. The resins of Rhubarb have already been alluded to in connection with Chrysophanic Acid. 19. *Rottlerin*, $C_{11}H_{10}O_3$ (*mallotoxin*, $C_{11}H_{10}O_3$, Perkin) is the name given by Anderson to a crystalline resin from Kamala (*Kamala*, B.P.), the minute glands that cover the capsules of *Rottlera tinctoria:* to this and, apparently, allied resins (*isorottlerin*, A. G. Perkin) Kamala owes its activity as an anthelmintic.

OLEO-RESINS.—1. "*Capsicin*," a term suggestive of a definite chemical substance, is a name somewhat unhappily accorded to an indefinite substance, an oleo-resin, obtained by digesting the alcoholic extract of Capsicum fruit (*Capsici Fructus*, B.P.) in ether and evaporating the clear ethereal fluid to dryness. Besides volatile oil and resin, capsicum fruits contain much fatty matter which Thresh states is chiefly free palmitic acid. (*See* also *Capsicine* and *Capsaicin*, in Index.) 2. *Copaiva* (*Copaiba*, B.P.) is a mixture of essential oil ($C_{15}H_{24}$), *copaivaöl*, $C_{20}H_{32}$ (Strauss), with 2 or more per cent. of brown soft resin, and 30 to 60 of a yellow dark crystalline resin consisting mostly of *copaivic acid* ($C_{20}H_{32}O_2$) with *oxycopaivic acid*, $C_{20}H_{28}O_3$ (Fuhling), and *metacopaivic* acid, $C_{22}H_{34}O_4$ (Strauss). Copaiva, containing about equal parts of this acid and of the oil, heated with a fourth of its weight of the official carbonate of magnesium, yields a transparent fluid, owing to the formation of copaivate of magnesium and solution of this soap in the essential oil. With an equal weight of the carbonate, enough soap is produced to take up the whole of the essential oil, and form a mass capable of being rolled into pills. A much smaller quantity of calcined magnesia, as might be expected, effects the same result; but more time, often several days, is required before complete reaction is effected. Quick-lime has a similar effect. Perhaps carbonate reacts more quickly because of its fine state of division and admixture of hydrate—in which case hydrates of calcium and magnesium may be expected to act better than the calcined preparations, and in much smaller quantity than carbonate of magnesium. Copaiva, unlike, 3, *Wood-oil*, or *Gurjun Balsam* (*Dipterocarpi Balsamum*, P.I.), a similar oleo-resin from the *Dipterocarpus turbinatus* (*D. Lævis*, P.I.) is almost entirely soluble in absolute alcohol and in petroleum spirit. Copaiva is often slightly fluorescent; Gurjun balsam is highly fluorescent. The stated analogy of Gurjun balsam to copaiva is borne out by its chemical composition; for by distillation it yields about 40 per cent. of an essential oil identical in composition with oil of copaiva, the non-volatile portion being resinous. The adulteration of copaiva with fixed oil is best detected by heating 20 or 30 drops in a capsule until all essential oil has evaporated. (Turpentine is betrayed by its odour during this evaporation.) The residue, copaiva resin, is brittle if pure, and more or less sticky or soft if fixed oil is present.

4. Oleo-resin of cubebs (*Oleo-Resina Cubebæ*, B.P.) is an ethereal extract of cubebs decanted from waxy matter (see *Piperine* and *Oil of Cubebs*). 5. *Elemi* (*Elemi*, B.P.) is an exudation from a tree growing in the Philippine Islands. It consists of volatile oil ($C_{10}H_{16}$) with 80 or more per cent. of two resins, the one ($C_{20}H_{32}O_2$) soluble in cold alcohol, the other, *Amyrin*, $(C_5H_8)_5H_2O$, almost insoluble, associated with *Amyric acid* $(C_5H_8)_7O_4$ (Buri). There is an α and a β amyrin, each having the formula $C_{30}H_{49}OH$ (Vesterberg). It also contains small quantities of two crystalline bodies soluble in water, *Bryoidin*, $(C_5H_8)_4 3H_2O$, and *Breidin* (Flückiger). The *Icacin* of Stenhouse and Groves is either identical with amyrin, or perhaps has the formula $(C_5H_8)_9H_2O$. All these bodies are probably hydrous terpenes. 6. *Wood-tar* (*Pix Liquida*, B.P.) is a mixture of several resinoid and oily bodies (amongst others Creasote, *see* Index) obtained by destructive distillation from the wood of *Pinus sylvestris* and other pines. When heated, it yields a terebinthinate oil and a residue of *pitch*. (*Earth Pitch*, or *Asphalte*, appears to be a partially oxidized petroleum.) *Oleum Cadinum*, B.P., "*Huile de Cade*," or *Juniper Tar Oil*, is the product of the similar destructive distillation of the *Juniperus Oxycedrus*. 7. *Turpentines.*—These oleo-resins have been mentioned in connection with *oil of turpentine*, their volatile, and *resin*, their fixed constituent. 8. *Common Frankincense* (*Thus Americanum*, B.P.) is the concrete turpentine of *Pinus tæda*. 9. *Canada Balsam* (*Terebinthina Canadensis*, B.P.) is largely gathered in the province of Quebec, and is the turpentine or oleo-resin of the Balm of Gilead Fir (*Abies balsamea*). 10. *Sumbul-root* (*Sumbul Radix*, B.P.) contains 9 per cent. of resin, to which probably it owes its stimulating properties. The resin consists of two parts, one soluble in ether and the other in alcohol, together with valerianic, sumbulic, and sumbuolic acids. By dry distillation it yields a blue oil. 11. *Oleo-Resin of Lupulin* (U.S.P.) is an ethereal extract of the yellow glandular powder (*Lupulinum*, B.P.) attached to the small nuts at the base of the scales which form the aggregate fruit of the Hop (*Humulus Lupulus*). It contains essential oil of hop (valerol, $C_6H_{10}O$), a terpene $C_{10}H_{16}$, oxidized oil or resin, bitter extract containing the hop-bitter, lupulinic acid ($C_{32}H_{50}O_7$), and tannic acid. It generally contains a good deal of earthy dust, but should not yield more than 15 per cent. of ash, and not more than 30 or 40 per cent. of matter insoluble in ether.

GUM-RESINS.—1. *Ammoniacum* (*Ammoniacum*, B.P.) is an exudation from the *Dorema Ammoniacum*. It contains nearly 20 per cent. of gum, a little volatile oil, and about 70 of resin ($C_{40}H_{50}O_9$—Johnston). 2. *Asafœtida* (*Asafœtida*, B.P.) formerly spelt *assafœtida*, is a gum-resin obtained, by incision, from the living root of *Ferula Narthex*. It contains from 50 to 70 per cent. of a resin which is partly *ferulaic acid* ($C_{10}H_{10}O_4$), 25 to 30 per cent. of gum (about two-thirds arabin, one-third bassorin, p. 127), a little vanillin, and 3 to 5 per cent. of volatile oil, which (Semmler) contains two sulphur compounds, $C_{17}H_{14}S$, and $C_{11}H_{20}S_2$, two terpenes $C_{10}H_{16}$, and a sesquiterpene $C_{15}H_{24}$. 3. *Euphorbium*, an old drug which is an emetic and purgative gum-resin, contains an amorphous active resin ($C_{20}H_{32}O_4$), crystalline *euphorbon* ($C_{26}H_{44}O_2$), and mucilage (Flückiger). 4. The ordinary or Siam *Gamboge* (*Gambogia*, B.P.) of European trade is obtained from the *Garcinia Hanburii*; the gamboge of India (*Cambogia Indica vel Mysoriensis*, P.I.) from *G. pictoria*. When of best quality, it contains about 20 per cent. of a gum, and 80 to 75 per cent. of a yellow resin termed *gambogic acid* ($C_{20}H_{24}O_4$). 5. *Galbanum* (*Galbanum*, B.P.) contains from 20 to 25 per cent. of gum, about 65 per cent. of resin ($C_{40}H_{54}O_7$), and 3 or 4 per cent. of volatile oil. Moistened with alcohol, and then with hydrochloric acid, galbanum yields a purple colour, due, probably, to the production and oxidation of resorcin. Galbanum heated for some time to 212° F. with hydrochloric acid, the liquid separated and shaken with ether or chloroform, and the latter evaporated, yields somewhat less than 1 per cent. of colourless acicular crystals of *umbelliferone* ($C_9H_6O_3$). "Umbelliferone is soluble in water; its solution exhibits, especially on addition of an alkali, a brilliant blue fluorescence which is destroyed by an acid. If a small fragment of galbanum is immersed in water, no fluorescence is observed, but it is immediately produced by a drop of ammonia. The same phenomenon takes place with asafœtida, and in a slight degree with ammoniacum; it is probably due to traces of umbelliferone pre-existing in those drugs. Umbelliferone is also produced from many other aromatic umbelliferous plants, as *Angelica*, *Levisticum*, and *Meum*, when their respective resins are submitted to dry distillation; also from the resin of *Daphne mezereum*. The fluorescence of umbelliferone may be beautifully shown by dipping some bibulous paper into water which has stood for an hour or two on lumps of galbanum, and drying it. A strip of this paper placed in a test-tube of water with a drop of ammonia will give a superb blue solution, instantly losing its colour on the addition of a drop of hydrochloric acid" (Flückiger and Hanbury). 6. *Myrrh* (*Myrrha*, B.P.), an exudation from the stem of *Balsamodendron myrrha*, contains about half its weight of soluble arabinoid gum, 10 per cent. of insoluble gum (probably bassorin), 2½ of volatile oil, isomeric with thymol and carvol (Köhler), and about 25 per cent. of resin (myrrhic acid). (For a note by R. H. Parker on the spurious gums imported with myrrh, *see* the *Pharmaceutical Journal* for July 17, 1880.) 7. *Olibanum* (P.I.). *Thus masculum* or *Arabian Frankincense* (from various species of *Boswellia*) is about one-third gum and nearly two-thirds resin ($C_{40}H_{30}O_6$), with a little hydrocarbon ($C_{10}H_{16}$) and oxidized hydrocarbon volatile oils. It has always been an important ingredient of *incense*—myrrh, storax, benzoin, and such fragrant combustible resinous substances, being other constituents. 8. *Scammony* (*see* Index).

Gum-resins need only to be finely powdered and rubbed in a mortar with water to yield a medicinal *emulsion*, in which the fine particles of resin are held in suspension by the aqueous solution of gum.

QUESTIONS AND EXERCISES.

What are the general chemical characters of volatile oils?—How do volatile oils usually differ chemically from fixed oils?—Describe the usual process by which volatile oils are obtained.—How does natural turpentine differ from turpentine of trade?—With what object is commercial turpentine rectified?—What is the chemical nature of india-rubber and gutta percha?—How is india-rubber *vulcanized* and converted into *ebonite* or *vulcanite*?—Mention the difference in composition between the volatile oils of *Anthemis nobilis* and *Matricaria Chamomilla*.—Give the systematic name for oil of horseradish.—State the general composition of the oils of lemon, lime, bergamot, citron, and cedra.—Name the constituents of oil of cloves.—In what respect does otto of roses differ from other oils?—What class of substances forms the chief part of oil of rue?—How is camphor-oil related to camphor?—In what respects do Borneo or Sumatra camphor and camphor oil differ from the corresponding products of Japan and China?—How may Borneol be artificially prepared?—How do resins occur in Nature? Distinguish between resins and camphors. Mention the points of difference of resins, oleo-resins, gum-resins, and balsams.—Name the sources of common resin or rosin.—Enumerate some official articles of which the active constituents are resins.—Give the distinguishing characters of Burgundy pitch.—What is the average proportion of oil and of resin in the so-called balsam of copaiva?—Explain the effect of carbonate of magnesium, magnesia, and lime on copaiva.—Why do ammoniacum, asafœtida, gamboge, galbanum, myrrh, and similar substances give an emulsion by mere trituration with water?

THE BENZENE SERIES OF HYDROCARBONS.

The Benzene or *Aromatic Series*, C_nH_{2n-6}.—This series is of great general interest. It yields, like other families of hydrocarbons, alcohols, haloid derivatives, aldehydes, acids, etc., obtained, however, as a rule by special rather than general methods. Just as the consecutive members of the paraffin series of hydrocarbons may be regarded as derived by the displacement of a hydrogen atom of the previous member by the methyl (CH_3) group, or of a hydrogen atom in methane by a paraffin radical, so the consecutive members of the benzene series may for convenience of study be viewed as obtained by the displacement of hydrogen atoms in *benzene* by paraffin radicals; as in the following examples:—

Benzene or Phenöene, C_6H_6.
Toluene, Benzöene, or Methylphenöene, C_7H_8 or $C_6H_5{\cdot}CH_3$.
Xylene or Dimethylphenöene, C_8H_{10} or $C_6H_4{\cdot}(CH_3)_2$.
Mesitylene or Trimethylphenöene, C_9H_{12} or $C_6H_3\,(CH_3)_3$.
Cymene or Methylpropylphenöene, $C_{10}H_{14}$ or $C_6H_4{\cdot}CH_3{\cdot}C_3H_7$.

It is, perhaps, desirable, as suggested by Odling, to designate the first member of this series by the name *phenöene* rather than *benzene*, as its hydrate is termed *phenol*, and its derivatives *phenyls*, *e.g.* phenylamine. Toluene (first obtained from balsam of tolu, hence the name) then becomes benzöene; from it benzoic acid is derived.

The members of the benzene series are *unsaturated* hydrocarbons. A molecule of benzene itself readily absorbs two, four, or six atoms of chlorine, these being added on to the benzene, forming what are termed *additive* compounds, as distinguished from the true substitutional compounds, in which the hydrogen atoms in benzene are actually substituted by chlorine, bromine, etc. The derivatives of benzene may more or less readily be re-converted into benzene, a fact supporting the close structural or constitutional relationship between the many benzenoid bodies.

Bodies having an aromatic odour are somewhat characteristic of the benzene series, hence the latter was originally termed the *aromatic series* of organic compounds.

Benzene or Benzol.

Benzene or Phenöene, C_6H_6 (commercially known as *Benzol*)*—Commercially it is obtained from the portion of coal-tar boiling below 100° C. It is partially purified by shaking successively with sulphuric acid, water, and caustic soda, and then redistilling; the product still containing large quantities of toluene and other impurities. If pure benzol is required, the liquid must be subjected to a freezing mixture, when the benzol crystallizes out, leaving some impurities in solution; the crystals are well drained. Bromine is then added to the liquid resulting from the melting of the crystals, until a permanent coloration results. The liquid is again washed with caustic soda, and distilled. Benzene boils at 81° C. It may be artificially produced by heating benzoic acid with lime, or by passing acetylene through red-hot tubes. It is a colourless, limpid, refractive liquid, having a specific gravity of 0·899 at 0° C. It is a powerful solvent of grease, and under the name of "Benzene Collas" was introduced by M. Collas in 1848 for cleansing purposes.

Benzene, when acted on by chlorine and bromine, in the presence of a little iodine, forms all derivatives from monochloro- and monobromo-benzene (C_6H_5Cl and C_6H_5Br) to hexachloro- and hexabromo-benzene (C_6Cl_6 and C_6Br_6). It also forms iodine and fluorine dorivatives, nitro-derivatives, etc.

Nitrobenzene (nitrobenzol, artificial oil of bitter almonds, or essence of mirbane), $C_6H_5NO_2$, is obtained by mixing fuming nitric acid, or a mixture of nitric and sulphuric acids, with benzene, the vessel being kept cool by immersion in water. It is a yellow liquid, heavier than water, having a strong odour of oil of bitter almonds, though of very different nature. (*Vide* "Oil of bitter almonds" in Index.) When acted on by nascent hydrogen, it yields aniline.

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[*] *Note.*—Care must be taken to distinguish between benzene, C_6H_6, and benzin, petroleum ether, benzolin, etc. (*Petroleum Spirit*, B.P.), which are mixtures of paraffin hydrocarbons of lower boiling points. *Benzin* (U.S.P.), C_5H_{12}: C_6H_{14}, and other hydrocarbons of the paraffin series having the boiling point of 122–140° F., requires six times its bulk of alcohol for solution, whereas benzene, C_6H_6, dissolves in less than its own bulk. Specific gravity of benzene about 0·850; of benzin about 0·700.

Aniline or *Phenylamine* or *Amidobenzene*, $C_6H_5NH_2$.*—Mix 13 parts of iron filings, 7 or 8 of the ordinary acetic acid, and 13 of nitro-benzene, in a large flask (with an upright condenser) placed in a water-bath, and set the whole aside for some time. After the mixture has digested for several hours, the supernatant liquid is poured off from the deposit of iron filings, and distilled in a current of steam. By this method the nitro-benzene yields, first, aniline, distilled over as a yellow oil, and afterwards a red oil, which is a mixture of azobenzene ($C_6H_5-N=N-C_6H_5$), hydrazobenzene ($C_6H_5-NH-NH-C_6H_5$) and azoxybenzene ($C_6H_5-N\overline{\diagdown O \diagup}N-C_6H_5$).

Aniline $C_6H_5NH_2$ (mixed with toluidine, $C_7H_7NH_2$), when acted on by arsenic acid, or chlorinated lime, produces *rosaniline*, $C_{20}H_{19}N_3$, whose salts and derivatives form most of the well-known aniline colours.

Constitution of Amines.—Amines are usually viewed as derivatives of ammonia, one, two, or three atoms of hydrogen being replaced by one, two, or three univalent organic radicals, or equivalents of radicals of higher quantivalence. The products were formerly known as amidogen (NH_2) bases, imidogen (NH) bases, and nitrile (N) bases; but are now termed primary, secondary, and tertiary amines. The class includes certain alkaloids.

Amides result when NH_2 displaces OH in acids. Acetic acid $= CH_3{\cdot}CO{\cdot}OH$; hence *acetamide* $= CH_3{\cdot}CO{\cdot}NH_2$. Aniline boiled with strong acetic acid yields *phenyl-acetamide*, or *acetanilide* (*Acetanilidum*, B.P.) or "*antifebrin*," a febrifuge, $C_6H_5{\cdot}NH{\cdot}C_2H_3O$ (a rival of "*antipyrin*," $C_{11}H_{12}N_2O$, *phenyl-dimethyl-pyrazolon*, $C_6H_5(CH_3)_2C_3HN_2O$, (*Phenazonum*, B.P.) from phenylhydrazine or aniline and aceto-acetic ether). *Monobrom-acetanilide*, $C_6H_4Br{\cdot}NH{\cdot}C_2H_3O$, is a sedative and febrifuge. *Phenacetin* (*Phenacetinum*, B.P.), or *para-acetphenetidin*, $C_6H_4{\cdot}OC_2H_5{\cdot}NH{\cdot}C_2H_3O$, is another febrifuge. *Phenocoll*, *amido-acet-phenetidin*, $C_6H_4{\cdot}OC_2H_5{\cdot}NHCOCH_2NH_2$. *Para-phenetol-carbamide* or *dulcin* is a body having a very powerful sweet taste, and proposed for use, like saccharin, in place of sugar.

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* Aniline may be obtained from indigo, hence its name, *anil*, being Portuguese for indigo.

Toluene, Benzöene, Methyl-phenöene, or Methyl-benzene (commercially known as *Toluol*), $C_6H_5CH_3$, forms the principal portion of coal tar boiling between 100–120° C.; it may be synthetically made by acting on monochlorobenzene and iodomethane by sodium.

$$C_6H_5Cl + CH_3I + Na_2 = C_6H_5CH_3 + NaI + NaCl.$$

It is also obtained by the dry distillation of tolu balsam. It is an inflammable, refractive liquid, boiling at 111° C. It may be directly oxidized to benzoic acid.

$$2C_6H_5CH_3 + 3O_2 = 2C_6H_5COOH + 2H_2O.$$

Having both a phenyl (C_6H_5) and a methyl (CH_3) group in its molecule, it forms two sets of isomeric derivatives: one (*a*) in which, by acting on toluene in the cold, the atoms of hydrogen are displaced in the phenyl group, and the other (*b*) by acting on boiling toluene, in which the atoms of hydrogen in the methyl group are displaced.*

$$a\left\{\begin{array}{l}\text{Tolyl chloride, or methylmonochlorobenzene, } C_6H_4Cl{\cdot}CH_3.\\ \text{Tolyl dichloride, or methyldichlorobenzene, } C_6H_3Cl_2CH_3.\\ \text{Tolyl trichloride, or methyltrichlorobenzene, } C_6H_2Cl_3CH_3.\end{array}\right.$$

$$b\left\{\begin{array}{l}\text{Monochloromethylbenzene, or benzyl chloride, } C_6H_5CH_2Cl.\\ \text{Dichloromethylbenzene, or benzyl dichloride, } C_6H_5CHCl_2.\\ \text{Trichloromethylbenzene, or benzyl trichloride, } C_6H_5CCl_3.\end{array}\right.$$

Dichloromethylbenzene when acted on by glacial acetic acid, and zinc chloride and water, produces benzoic aldehyde, C_6H_5COH (Jacobson). By acting on trichloromethylbenzene by water in sealed tubes, benzoic acid results.

$$C_6H_5CCl_3 + 2H_2O = C_6H_5COOH + 3HCl.$$

Cymene, $C_{10}H_{14}$.—Propylmethylbenzene, $C_6H_4(CH_3)(C_3H_7)$ occurs in several volatile oils, and is readily obtained by the removal of hydrogen from the terpenes ($C_{10}H_{16}$) of those oils. Many of the members of the benzene series have an aromatic odour, hence the synonym *aromatic series*.

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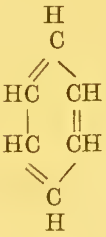
* *Note.*—"Benzyl" is the name given to the derivatives of benzöene when substitution takes place in the methane nucleus, "tolyl" when in the phenoëne nucleus.

CONSTITUTION OF THE BENZENE SERIES.

The fact that benzene forms three additive derivatives with chlorine, $C_6H_6Cl_2$, $C_6H_6Cl_4$, and $C_6H_6Cl_6$, 1 molecule uniting with not more than 6 atoms of chlorine, and that it affords no isomeric monosubstitution derivatives (but only one toluene, $C_6H_5CH_3$, one benzoic acid, C_6H_5COOH, and one only of all such derivatives), led Kekulé to represent benzene by the following figure (*a*), in which each atom of carbon is assumed to be "linked" to adjacent atoms of carbon by three-fourths of its affinity, the remaining fourth of its attraction being exerted towards the equivalent attraction of another atom, thus (*figure a*) :—

Fig. a.



Benzene.

Fig. d.

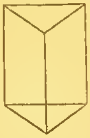


Fig. b.

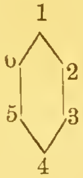


Fig. e.

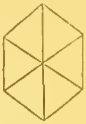
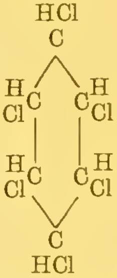


Fig. c.



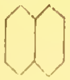
Hexachlorobenzene.

In a *monosubstitution derivative* such as chlorobenzene, C_6H_5Cl, no matter where the atom of chlorine be placed, it bears the same relation to the atoms of hydrogen; hence there can be *only one variety* of such a derivative. The experimental evidence of the truth of this inference is as follows. Displace H in benzene by another radical X and obtain C_6H_5X. In the latter displace H by Y and obtain C_6H_4XY. Now displace X by H and obtain C_6H_5Y. Lastly displace Y by X and obtain C_6H_5X. The first C_6H_5X and the last C_6H_5X are identical in properties, yet manifestly the latter X is in a different position to the first X; whence we conclude that actual position matters nothing if relative position is unchanged. Such hydrocarbons are *symmetrical*. Such mono-X compounds are *unsymmetrical*. Further displacements of H by X in C_6H_5X results in *more than one variety* of C_4H_4XX. In dichlorobenzene, $C_6H_4Cl_2$, the atoms of chlorine may (representing, for the moment, benzene by a hexagonal figure (*b*), and assuming that the carbon atoms are at the angles) be placed either at 1 and 2, 1 and 3, or 1 and 4, the chlorine atoms being either near to each other, separated by one carbon atom or by two carbon atoms. So with other *di-derivatives.* In trichlorobenzene, $C_6H_3Cl_3$, the atoms of chlorine may be placed at 1, 2, and 3; 1, 2, and 4; or 1, 3, and 5; 1, 2, and 4 being the same as 1, 3, and 4; 1, 2, and 3, the same as 1, 6, and 5, etc.; that is to say, the chlorine atoms must all three be near to each other, or two near to each other, and one be separated, or all three be separated as far from each other as possible in the molecule. So with other *tri-derivatives.* Hence, theoretically, there can only be three isomeric di- and trichlorobenzenes; which has been verified by experiment. For other illustrations, and for nomenclature, *see* page 542.

In the *additive compounds* a second quarter of the affinity of the carbon atoms for each other is freed, so to say, for exertion towards the added chlorine atoms (*figure c*). The mind may be aided in forming an idea of the constitution of molecules like benzene by other figures such as the prism (*d*) or wheel-like hexagon (*e*); devices all of which embody the idea of the interdependence of each atom of the molecule on every other atom, the idea conveyed by the linkages, not only of a series of links of an open chain as pictured on previous pages, but of a chain without terminal links, a continuous, or closed, or endless chain—the open chain with its ends linked together and even sometimes also having cross linkages.

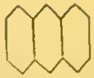
OTHER SERIES OF HYDROCARBONS.

The Naphthalene Series, C_nH_{2n-12}.



Naphthalene, $C_{10}H_8$, is the chief member. It is a white crystalline body, existing in coal-tar. By oxidation it yields phthalic acid, $C_6H_4(COOH)_2$, the anhydride of which, $C_6H_4(CO)_2O$, fused with phenol, forms *phenol-phthalein* (B.P.), an alkalimetric indicator. With other phenols various coloured bodies are produced; for example, with resorcinol *fluorescin*, which, treated with bromine, gives *eosin.* Such bodies are termed *phthaleins.* Naphthalene is employed for increasing the luminosity of coal-gas. Of the two *naphthyl-alcohols*, or *naphthols*, or *monoxynaphthalenes*, $C_{10}H_7(OH)$ α & β, *beta-naphthol* is the well-known powerful antiseptic.

The Anthracene Series, C_nH_{2n-18}.



Anthracene, $C_{14}H_{10}$, is the only noteworthy member of this series, its importance being due to the fact that *artificial madder*, or *alizarin*, is formed from it by the following reactions:—Anthracene is first oxidized to anthraquinone by the influence of nascent oxygen. By acting on anthraquinone with fuming sulphuric acid, it is easily converted into a derivative, which yields alizarate of potassium when fused with caustic potash.

Chrysophanic acid ($CH_3C_{14}H_5(OH)_2O_2$) and the *aloins* are related to anthraquinone; chrysophanic acid being a dihydroxy-derivative of methylanthraquinone, and the aloins ($C_{16}H_{18}O_7$) yielding on oxidation aloxanthin or tetrahydroxymethylanthraquinone.

Aloins.

Aloins.—The aloes of pharmacy (*Aloe Barbadensis*, B.P., and *Aloe Socotrina*, B.P.) is an evaporated juice, doubtless much altered by the temperature to which it is subjected. It contains a yellow crystalline substance, *Aloin* (B.P.), slightly varying chemically, but not medicinally, as derived from the respective species of aloes. Aloin is not very soluble in cold water or spirit, but readily soluble in the hot fluids. Dissolved in alkalies it rapidily absorbs oxygen, but it is not readily altered in neutral or acidified solutions.

Aloin may readily be obtained from either kind of aloes by warming with three or four times its weight of amylic alcohol; pouring off the solution; allowing it to stand for a few hours to crystallize; and washing the deposited aloin with ether or bisulphide of carbon to remove resinoid matters.

Barbaloin.—This substance, first obtained by T. and H. Smith, occurs in minute crystals in Barbadoes aloes. It yields, by the action of bromine and chlorine, substitution compounds. Nitric acid dropped upon it produces a red colour which soon fades. Boiled for some time with strong nitric acid, barbaloin gives, together with oxalic and picric acids, a yellow substance, chrysammic acid, which furnishes beautiful red salts (Tilden). Anthracene ($C_{14}H_{10}$) has been obtained by deoxidation of barbaloin.

Nataloin.—This body was discovered by Flückiger in Natal aloes. It crystallizes readily in rectangular plates, either from spirit or from water. No bromine or chlorine substitution derivatives have yet been formed, but an acetyl compound has been analysed (Tilden). Nataloin moistened with nitric acid gives a red coloration which does not fade. When boiled with nitric acid it yields no chrysammic, but only oxalic and picric acids.

Socaloin or *Zanaloin*.—Histed and Flückiger have shown that Socotrine or Zanzibar aloes yields an aloin distinct from those just described. It forms tufted acicular prisms. Nitric acid scarcely alters the colour of socaloin. Neither socaloin nor barbaloin afford any colour when vapour from a glass rod moistened with nitric acid is brought near to a drop of oil of vitriol containing a minute fragment of the aloin, while nataloin gives rise to a blue coloration.

Analysis.—To aloin or powdered aloes on a white plate add strong nitric acid. *No colour* = socaloin. *Crimson colour* = nataloin or barbaloin. To another portion add strong sulphuric acid and vapour of nitric acid. *A blue colour* = nataloin. *No blue colour* = barbaloin.

For other methods of distinguishing the aloins, and other allied bodies, *see* a paper on Aloins by Cripps and Dymond, *Pharmaceutical Journal*, February 7th, 1885.

E. von Sommaruga and Egger ("Pharmacographia") arrived at the conclusion that the aloins form an homologous series, and that they have the composition indicated in the following formulæ: Socaloin, $C_{15}H_{16}O_7$; Nataloin, $C_{16}H_{18}O_7$; Barbaloin, $C_{17}H_{20}O_7$. Tilden's subsequent experiments indicate, however, that barbaloin ($C_{16}H_{18}O_7$) and socaloin ($C_{16}H_{18}O_7$) are isomeric in the anhydrous state, but that socaloin and its derivatives in the hydrous condition contain more water of crystallization than barbaloin. Nataloin ($C_{16}H_{18}O_7$) seems to be isomeric with the others, but is less soluble, and does not yield either chrysammic acid or chloro- or bromo-derivatives ($C_{16}H_{15}Cl_3O_7$; $C_{16}H_{15}Br_3O_7$). The acetyl-derivatives appear to have the formula, $C_{16}H_{15}(C_2H_3O)_3O_7$. According to Grænewold the formula for the aloin from the aloes of Barbadoes and Curaçoa is $C_{16}H_{16}O_7$, and that from Natal aloes $C_{24}H_{26}O_{10}$.

QUESTIONS AND EXERCISES.

What is the formula of benzene? How is it artificially and commercially prepared?—Draw out an equation explanatory of the production of aniline.—What is the relation between toluene and benzoic acid?—

Give the formulæ of naphthalene and anthracene.—Explain by equations the production of alizarin or artificial madder.—Give tests for distinguishing the aloins.

The student is referred to the accompanying table for a general view of the relations of four series of hydrocarbons (the paraffin, benzene, naphthalene, and anthracene series) to each other. Three members of the paraffin series are shown, two of the benzene series, and one each of the naphthalene, and anthracene series. Beneath each hydrocarbon are given its chief derivatives. A glance along the table shows the relation of these derivatives to each other.

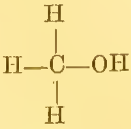
ALCOHOLS.

Alcohols are those bodies in which one or more hydrogen atoms of the hydrocarbons are displaced by one or more hydroxyl (OH) groups, forming (*a*) monhydroxyl derivatives, (*b*) dihydroxyl derivatives, etc.; they are in fact hydrates of unsaturated or radical hydrocarbons, just as caustic potash and slaked lime are hydrates of potassium and calcium, thus:—

C_2H_5OH Ethyl hydrate.	KHO, or KOH Potassum hydrate.
$C_2H_4(OH)_2$ Ethylene hydrate, or glycol.	$Ca(HO)_2$ Calcium hydrate.
$C_3H_5(OH)_3$ Glyceric hydrate, or glycerine.	$Bi(OH)_3$ Bismuth hydrate.

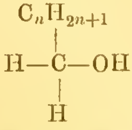
a. Monhydroxyl Derivatives of Paraffins.

The Ethylic Series of Alcohols, $C_nH_{2n+1}OH$.—The alcohols, or *carbinols* (Kolbe), are *primary*, *secondary*, or *tertiary*, according as one, two, or three atoms of hydrogen in the first (or hydrogen) member of the series (methylic alcohol or *carbinol* itself, CH_3OH) are displaced by one, two, or three atoms of any radical having the general formula C_nH_{2n+1}. Thus:—



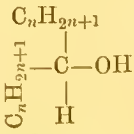
$$\begin{array}{c} H \\ | \\ H—C—OH \\ | \\ H \end{array}$$

Carbinol.



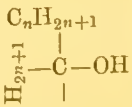
$$\begin{array}{c} C_nH_{2n+1} \\ | \\ H—C—OH \\ | \\ H \end{array}$$

Typical primary carbinol.



$$\begin{array}{c} C_nH_{2n+1} \\ | \\ C_nH_{2n+1}—C—OH \\ | \\ H \end{array}$$

Typical secondary carbinol.



$$\begin{array}{c} C_nH_{2n+1} \\ | \\ C_nH_{2n+1}—C—OH \\ | \\ C_nH_{2n+1} \end{array}$$

Typical tertiary carbinol.

Synoptical Table showing the Relations between the Principal Members of the Paraffin, Benzene, Naphthalene, and Anthracene Series of Hydrocarbons and between their Deriva

Hydrocarbon ...	CH_4	**Methane.**	C_2H_6 or CH_3CH_3	**Ethane** or Methylmethane	C_3H_8 or $C_2H_5{\cdot}CH_3$	**Propane** or Ethyl-methane	C_6H_6	**Phenoëne** or **Benzene**	C_7H_8 or $C_6H_5{\cdot}CH_3$	**Benzoëne, Toluene** or Methylphenoëne	$C_{10}H_8$	**Naph**
Alkyl Salt or Ethereal Salt, Etc.	CH_3Cl	Methyl chloride or Chloromethane	C_2H_5Cl or CH_3CH_2Cl	Ethyl chloride or Chloroethane	C_3H_7Cl or $C_2H_5{\cdot}CH_2Cl$	Propyl chloride or Chloropropane	C_6H_5Cl	Phenyl chloride or Chlorobenzene	C_7H_7Cl or $C_6H_4Cl{\cdot}CH_3$ $C_6H_5{\cdot}CH_2{\cdot}Cl$	Chlorotoluenes Tolyl chloride Benzyl chloride	$C_{10}H_7Cl$	Napht Chlor
	CH_3NO_2	Methyl nitrite or Nitromethane	$C_2H_5NO_2$ or $CH_3CH_2NO_2$	Ethyl nitrite or Nitroethane	$C_3H_7NO_2$ or $C_2H_5CH_2{\cdot}NO_2$	Propyl nitrite or Nitropropane	$C_6H_5NO_2$	Phenyl nitrite or Nitrobenzene	$C_7H_7NO_2$ or $C_6H_4{\cdot}NO_2{\cdot}CH_3$ $C_6H_5{\cdot}CH_2NO_2$	Nitrotoluenes Tolyl nitrite Benzyl nitrite	$C_{10}H_7NO_2$	Nitro
Amine	CH_3NH_2	Methylamine	$C_2H_5NH_2$ or $CH_3CH_2NH_2$	Ethylamine	$C_3H_7NH_2$ or $C_2H_5CH_2{\cdot}NH_2$	Propylamine	$C_6H_5NH_2$	Phenylamine or Aniline	$C_7H_7NH_2$ or $C_6H_4NH_2{\cdot}CH_3$ $C_6H_5{\cdot}CH_2NH_2$	Tolylamine Benzylamine	$C_{10}H_7NH_2$	Naph
Monhydric Alcohol	CH_3OH or HCH_2OH	Methyl alcohol or Carbinol	C_2H_5OH or CH_3CH_2OH	Ethyl alcohol or Methylcarbinol	C_3H_7OH or $C_2H_5{\cdot}CH_2{\cdot}OH$ $(CH_3)_2CH{\cdot}OH$	Primary Propyl Alcohol or Ethyl carbinol Secondary Propyl Alcohol or Dimethyl carbinol	C_6H_5OH	Phenyl alcohol or Phenol	$C_7H_7{\cdot}OH$ or $C_6H_4{\cdot}OH{\cdot}CH_3$ $C_6H_5CH_2OH$	Tolyl alcohol or Cresol Benzyl alcohol or Phenyl carbinol	$C_{10}H_7OH$	Napht Nap
Dihydric Alcohol	... ...	... ...	$C_2H_4(OH)_2$ or $CH_2OH{\cdot}CH_2OH$	Ethylene glycol or Glycol	$C_3H_6(OH)_2$ or $C_2H_4OH{\cdot}CH_2OH$	Propylene Glycol	$C_6H_4(OH)_2$	Pyrocatechin Resorcin Hydroquinone .	$C_7H_6(OH)_2$ or $C_6H_4{\cdot}OH{\cdot}CH_2OH$	Salicyl alcohol, Saligenol or Hydroxybenzyl alcohol	$C_{10}H_6(OH)_2$	Napht Dihy
Trihydric Alcohol	... ...	... ...	... ...	... ...	$C_3H_5(OH)_3$ or $C_2H_3(OH)_2CH_2OH$	Glycerol or Glycerin	$C_6H_3(OH)_3$	Pyrogallol or Pyrogallic acid	... ...	... ...	$C_{10}H_5(OH)_3$	Trihy
Aldehyde	CH_2O or $H{\cdot}CO{\cdot}H$	Formic aldehyde	C_2H_4O or $CH_3{\cdot}CO{\cdot}H$	Acetic aldehyde	C_3H_6O or $C_2H_5{\cdot}CO{\cdot}H$	Propionic aldehyde	... ...	... ...	C_7H_6O or $C_6H_5{\cdot}CO{\cdot}H$	Benzoic aldehyde		
Ketone	... ...	... ...	... ...	... ...	C_3H_6O or $CH_3{\cdot}CO{\cdot}CH_3$	Acetone or Dimethyl ketone						
Nitrile	HCH_2CN	Acetonitrile or Methyl cyanide	C_2H_5CN or CH_3CH_2CN	Propionitrile or Ethyl cyanide	C_3H_7CN or $C_2H_5CH_2CN$	Butyronitrile or Propyl cyanide (primary)	C_6H_5CN	Benzonitrile or Phenyl cyanide	C_7H_7CN or $C_6H_5{\cdot}CH_2{\cdot}CN$	Benzyl cyanide	$C_{10}H_7CN$	Napht Napht
Monobasic Acid (Monohydric)	$H{\cdot}CO{\cdot}OH$*	Formic acid	$C_2H_4O_2$ or $CH_3{\cdot}CO{\cdot}OH$	Acetic acid or Methyl-formic acid	$C_3H_6O_2$ or $C_2H_5{\cdot}CO{\cdot}OH$	Propionic acid or Ethyl-formic acid	... ...	... ...	C_7H_6O or $C_6H_5{\cdot}CO{\cdot}OH$	Benzoic acid or Phenyl-formic acid		
Monobasic Acid (Dihydric)	$OH{\cdot}CO{\cdot}OH$†	Hydroxyformic acid or carbonic acid	$C_2H_4O_3$ or $CH_2OH{\cdot}CO{\cdot}OH$	Glycollic acid or Hydroxyacetic acid	$C_3H_6O_3$ or $C_2H_4(OH){\cdot}CO{\cdot}OH$	Lactic acid or Hydroxypropionic acid	... ...	... ...	$C_7H_6O_3$ or $C_6H_4OH{\cdot}CO{\cdot}OH$	Salicylic acid or Hydroxybenzoic acid		
Monobasic Acid (Trihydric)	... ...	... ...	... ...	... ...	$C_3H_6O_4$ or $C_2H_3(OH)_2{\cdot}CO{\cdot}OH$	Glyceric or Dihydroxypropionic acid	... ...	... ...	$C_7H_6O_4$ or $C_6H_3(OH)_2{\cdot}CO{\cdot}OH$	Dihydroxybenzoic acid		
Dibasic Acid ...	... ...	... ...	$C_2O_4H_2$ or $COOH{\cdot}COOH$	Oxalic acid	$CH_2(CO{\cdot}OH)_2$	Malonic acid ‡						
Ether	$(CH_3)_2O$	Methyl ether	$(C_2H_5)_2O$	Ethyl ether	$(C_3H_7)_2O$	Propyl ether	$(C_6H_5)_2O$	Phenyl ether				

* The nitrile of Formic acid or Formonitrile is HCN (Hydrocyanic acid). † The existence of $OH{\cdot}CO{\cdot}OH$ is not definitely proved. The association of two OH groups with one atom of carbon is unusual. *See p.* 366. ‡ This cannot be obtained by direct oxidation of Propylene glycol. *Note.*—Th

[*To face p.* 520.]

pal Members of the Paraffin, Benzene, Naphthalene, and Anthracene Series of Hydrocarbons and between their Derivatives.

	Propane or Ethyl-methane	C_6H_6	**Phenoëne** or **Benzene**	C_7H_8 or $C_6H_5{\cdot}CH_3$	**Benzoëne, Toluene** or Methylphenoëne	$C_{10}H_8$	**Naphthalene**	$C_{14}H_{10}$	**Anthracene**
Cl	Propyl chloride or Chloropropane	C_6H_5Cl	Phenyl chloride or Chlorobenzene	C_7H_7Cl or $C_6H_4Cl{\cdot}CH_3$ $C_6H_5{\cdot}CH_2{\cdot}Cl$	Chlorotoluenes Tolyl chloride Benzyl chloride	$C_{10}H_7Cl$	Naphthalene chloride Chloronaphthalene	$C_{14}H_9Cl$	Anthracene chloride Chloroanthracene
$_2{\cdot}NO_2$	Propyl nitrite or Nitropropane	$C_6H_5NO_2$	Phenyl nitrite or Nitrobenzene	$C_7H_7NO_2$ or $C_6H_4{\cdot}NO_2{\cdot}CH_3$ $C_6H_5{\cdot}CH_2NO_2$	Nitrotoluenes Tolyl nitrite Benzyl nitrite	$C_{10}H_7NO_2$	Nitronaphthalene		
$_2{\cdot}NH_2$	Propylamine	$C_6H_5NH_2$	Phenylamine or Aniline	$C_7H_7NH_2$ or $C_6H_4NH_2{\cdot}CH_3$ $C_6H_5{\cdot}CH_2NH_2$	Tolylamine Benzylamine	$C_{10}H_7NH_2$	Naphthylamine		
$CH_2{\cdot}OH$ $CH{\cdot}OH$	Primary Propyl Alcohol or Ethyl carbinol Secondary Propyl Alcohol or Dimethyl carbinol	C_6H_5OH	Phenyl alcohol or Phenol	$C_7H_7{\cdot}OH$ or $C_6H_4{\cdot}OH{\cdot}CH_3$ $C_6H_5CH_2OH$	Tolyl alcohol or Cresol Benzyl alcohol or Phenyl carbinol	$C_{10}H_7OH$	Naphthylic alcohol or Naphthol	$C_{14}H_9{\cdot}OH$	Anthracene alcohol Anthrol
$H{\cdot}CH_2OH$	Propylene Glycol	$C_6H_4(OH)_2$	Pyrocatechin Resorcin Hydroquinone	$C_7H_6(OH)_2$ or $C_6H_4{\cdot}OH{\cdot}CH_2OH$	Salicyl alcohol, Saligenol or Hydroxybenzyl alcohol	$C_{10}H_6(OH)_2$	Naphthaquinol or Dihydroxynaphthalene	$C_{14}H_8(OH)_2$	Anthraquinol or Dihydroxyanthracene
$H)_2CH_2OH$	Glycerol or Glycerin	$C_6H_3(OH)_3$	Pyrogallol or Pyrogallic acid	... ...	... ...	$C_{10}H_5(OH)_3$	Trihydroxynaphthalene		
	Propionic aldehyde	... ...	... ...	C_7H_6O or $C_6H_5{\cdot}CO{\cdot}H$	Benzoic aldehyde				
H_3	Acetone or Dimethyl ketone								
CN	Butyronitrile or Propyl cyanide (primary)	C_6H_5CN	Benzonitrile or Phenyl cyanide	C_7H_7CN or $C_6H_5{\cdot}CH_2{\cdot}CN$	Benzyl cyanide	$C_{10}H_7CN$	Naphthonitrile Naphthylic cyanide		
OH	Propionic acid or Ethyl-formic acid	... ...	... ...	C_7H_6O or $C_6H_5{\cdot}CO{\cdot}OH$	Benzoic acid or Phenyl-formic acid				
${\cdot}CO{\cdot}OH$	Lactic acid or Hydroxypropionic acid	... ...	... ...	$C_7H_6O_3$ or $C_6H_4OH{\cdot}CO{\cdot}OH$	Salicylic acid or Hydroxybenzoic acid				
$_2{\cdot}CO{\cdot}OH$	Glyceric or Dihydroxypropionic acid	... ...	... ...	$C_7H_6O_4$ or $C_6H_3(OH)_2{\cdot}CO{\cdot}OH$	Dihydroxybenzoic acid				
	Malonic acid ‡								
	Propyl ether	$(C_6H_5)_2O$	Phenyl ether						

The association of two OH groups with one atom of carbon is unusual. *See p.* 366. ‡ This cannot be obtained by direct oxidation of Propylene glycol. *Note.*—This Table is a slight extension of one compiled by Dunstan.

The primary oxidize their CH_2OH group to aldehydes (bodies containing the aldehydic group COH) and acids (bodies having the group COOH or *carboxyl*); the secondary oxidize their CHOH group to form a ketone (a body having *carbonyl*, CO″, as a group, as acetone CH_3–CO–CH_3), and by further oxidation break up, forming bodies with less carbon units than the original alcohol; while the tertiary yield a ketone and an acid. The primary alcohols alone are of practical interest to medical and pharmaceutical students. The tertiary alcohols are said to be depressants instead of stimulants. For examples of primary, secondary and tertiary alcohols, *see* page 534.

General method of preparing Primary Alcohols.—By acting on the monochloro-derivatives of a paraffin by acetate of potassium or silver, an ethereal salt (acetate) is produced, which when saponified with caustic potash yields the alcohol. For instance,—

$$\underset{\substack{\text{Ethylic}\\\text{chloride.}}}{C_2H_5Cl} + \underset{\substack{\text{Silver}\\\text{acetate.}}}{AgC_2H_3O_2} = \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{C_2H_5C_2H_3O_2} + \underset{\substack{\text{Silver}\\\text{chloride.}}}{AgCl}$$

$$\underset{\substack{\text{Ethylic}\\\text{acetate.}}}{C_2H_5C_2H_3O_2} + \underset{\substack{\text{Potassium.}\\\text{hydrate.}}}{KHO} = \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{C_2H_5OH} + \underset{\substack{\text{Acetate of}\\\text{potassium.}}}{KC_2H_3O_2}$$

If the chloro-derivatives were directly acted upon by the hydrate of potassium, hydrocarbons of the olefine or acetylene series would result.

The chief primary alcohols are, however, otherwise obtained.

Note on Nomenclature.—The student will perceive that such names as those in the following set are used indifferently:—ethylic acetate, ethyl acetate, acetate of ethyl, acetic ether.

Methylic Alcohol.

Methyl (μέθυ, *methu*, wine, and ὕλη, *ule*, wood) Alcohol or Carbinol, CH_3OH or HCH_2OH (*Pyroxylic Spirit* or *Wood Naphtha*), is a product of the destructive distillation of wood, and is now obtained in large quantities as a by-product in the manufacture of beet sugar in France. By oxidation it yields formic acid (*see* page 401).

Methylated Spirit.—Spirit of wine containing 10 per cent.

of wood-spirit constitutes ordinary *methylated spirit*, a spirit issued duty free, for the use of manufacturers, the methylic alcohol, etc., not interfering with technical applications. From its nauseous taste and odour, however (not due to methyl alcohol, but to tarry bodies), it cannot take the place of gin, brandy, or other spirit; hence, while industry is benefited, intemperance is discouraged and the revenue not injured.

Detection of Methylic Alcohol in presence of Ethylic Alcohol.—Three or four methods have been proposed for the detection of methylated spirit in various liquids; that most used by pharmacists is by J. T. Miller. For the application of the test to tinctures and similar spirituous mixtures, some of the spirit is first separated by distilling off a drachm or so from about half an ounce of the liquid placed in a small flask or test-tube having a long bent tube attached. Into a similar apparatus put 30 grains of powdered red chromate of potassium, half an ounce of water, 25 minims of strong sulphuric acid, and 30 or 40 minims of the spirit to be tested. Set the mixture aside for a quarter of an hour, and then distil nearly half a fluid ounce. Place the distillate in a small dish, add a very slight excess of carbonate of sodium, boil down to about a quarter of an ounce, add enough acetic acid to impart a distinct but feeble acid reaction, pour the liquid into a test-tube, add a grain of nitrate of silver dissolved in about 30 drops of water, and heat gently for a couple of minutes. If the liquid then merely darkens a little, but continues quite translucent, the spirit is free from methylic alcohol; but if a copious precipitate of dark-brown or black metallic silver separates, and the tube, after being rinsed out and filled with clean water, has a distinct film of silver, which appears brown by transmitted light (best seen by holding it against white paper), the spirit is methylated. The experiments are best performed by daylight.

Explanation.—This test depends for its action on the reducing-powers of formic acid. In the above operation the ethylic alcohol becomes oxidized to acetic acid (the natural acid of the ethyl series), which does not reduce silver salts, a minute quantity only of formic acid being produced, while the methylic alcohol yields formic acid (the natural acid of the methyl series) in a comparatively large quantity. Aldehyde, which is also a reducing agent, is simultaneously produced, but removed in the subsequent ebullition with carbonate of sodium.

Methylated Sweet Spirit of Nitre.—The preparation of spirit of nitrous ether from methylated spirit is illegal in Great Britain, and, probably, is very rarely practised. For the detection of methylic alcohol in this liquid, Mr. Miller suggests the following modification of the foregoing process.

Shake about an ounce of the sample with 20 or 30 grains of anhydrous carbonate of potassium, and, if needful, add fresh portions of the salt until it ceases to be dissolved, then pour off the supernatant spirit. This serves to neutralize acid and to remove water, of which an abnormal quantity may be present. Introduce half a fluid ounce of the spirit into a small flask ; add 150 grains of anhydrous chloride of calcium in powder, and stir well together ; then, having connected the flask with a condenser, place it in a bath of boiling water, and distil a fluid drachm and a half, or continue the distillation until scarcely anything more comes over. The operation is rather slow, but needs little attention, and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering substances, while in the retort there remains a non-volatile compound of chloride of calcium and methylic alcohol, if the latter be present. Now add to the contents of the flask a fluid drachm of water, which decomposes the compound just referred to, and draw over the half-drachm of spirit required for testing. Then proceed as described in the foregoing paragraphs.

Ethylic Alcohol.

Ethyl Alcohol, or Methyl Carbinol, commonly called simply *Alcohol* (C_2H_5OH, or CH_3CH_2OH).—It is a colourless liquid, having a boiling point of 173·6° F. and sp. gr. 0·7935. Ethyl alcohol may be obtained by passing ethylene into strong sulphuric acid. The product, ethylhydrogen sulphate, when distilled with water, yields alcohol:—

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O = C_2H_5HO + H_2SO_4$$

On the large scale alcohol is produced by fermentation. All fermented bread retains a little alcohol, sometimes as much as 1 in 400.

Formation of Alcohol.—Ferment two or three grains of sugar by dissolving it in a test-tube full of water, adding a little yeast (*Cerevisiœ Fermentum*, B.P.), or a piece of the so-called German or dried yeast, and setting the whole aside for several hours in a warm place at a temperature of 75° to 85° F.; carbonic acid gas is evolved, and, if the tube be inverted in a small dish containing water, may be collected in the upper part of the tube and subsequently tested: the solution contains alcohol. If the experiment be made on larger quantities (four ounces of sugar, one of yeast, and a pint of water) the fermented liquid should be distilled, one-half being collected, shaken with a little lime, soda, or potash to neutralize any acetic acid and decompose ethereal salts, and again distilled till one-half has passed over; the product is dilute spirit of wine. It may be still further concentrated or rectified by repeating this process of *fractional distillation*, the separate fractions being redistilled, then fractions having fairly near boiling-points being mixed and again distilled, and so on until the ethylic alcohol, the other alcohols (chiefly amylic alcohol), and the water, having had the cohesive tendencies of their molecules thus overcome, are separated from each other. The heads of stills can be so adapted, especially on the large scale, as to condense and deliver at once the substances having different boiling-points.

Fermentation.—The act of fermentation is commonly the result of or rather accompaniment of some vital action. *Alcoholic fermentation* would appear to be always attended by or to attend development of life and free multiplication of cellular structure. It follows the development of the fungus already referred to as constituting the chief active part of yeast, the *saccharomyces cerevisiæ*. In the presence of this fungus, with small quantities of phosphates and albumenoid matter, *glucose* is converted into alcohol and carbonic acid gas, together with small portions of glycerine, succinic acid, and other substances. Yeast also contains a soluble ferment, *invertase*, analogous to diastase, which is capable of converting sucrose into glucose. Therefore if yeast be used, *sucrose* or cane sugar may be converted into carbonic acid gas and alcohol, the soluble ferment first converting the sucrose, not itself fermentable by the saccharomyces, into glucose.

$$\underset{\text{Grape sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Not more than 20 per cent. by weight of alcohol can be obtained in a fermenting fluid, for more than this proportion prevents fermentation.

Other kinds of fermentation, arising from the action of special ferments which have not received in all cases distinctive names, are the following:— *Viscous* or *Mannitic fermentation*, which occurs when beer or saccharine juices, such as that of beet-root, become "ropy." Gum, mannite, and carbonic acid gas, are produced. For *Lactic* and *Butyric fermentations, see* "Lactic Acid." *Putrefactive fermentation* occurs when a liquid containing albumenoid matter is exposed to the air. Infusoria appear in the liquid, using up the dissolved oxygen, and the ferments of the genus *vibrio* are developed. These are protected from oxygen, which is fatal to them, by a thin surface layer crowded with bacteria—small rod-like organisms having powers of locomotion. The vibrionic action, or putrefaction, proceeds with evolution of sulphuretted hydrogen, together with other gases having unpleasant odours and of complex chemical constitution. For *Acetic fermentation, see* "Acetic Acid." For *Ammoniacal fermentation, see* "Urine."

Fermentation by certain Soluble Albumenoids.—For the conversion of starch into sugar by diastase, *see* "Starch"; of amygdalin into benzoic aldehyde, hydrocyanic acid, and glucose by emulsin, *see* "Amygdalin"; of salicin into saligenin and glucose, *see* "Salicin"; of myronate of potassium into sulphocyanate of allyl, etc., by myrosin, *see* "Mustard"; of cane-sugar into grape-sugar by the soluble ferment in yeast, *see* the foregoing paragraphs. Many soluble ferments or *hydrolysts* occur in the germinating seeds and other parts of plants, and play an important part in nutrition.

Alcoholic Fermentation.—The chief reaction results, as already stated, in the formation of alcohol and carbonic acid gas, though 3 per cent. of glycerine, 0·5 of succinic acid, and traces of several other substances are simultaneously produced (*vide* "Fousel Oil" in Index). By this reaction is formed the spirit of the various kinds of wine, beer, and liqueurs, such as Orange Wine (*Vinum Aurantii*, B.P.), made "by the fermentation of a saccharine solution to which the fresh peel of the bitter orange has been added;" Sherry Wine (*Vinum Xericum*, B.P.), the fermented juice of the grape; Bay Rum, or Spirit of Myrcia (*Spiritus Myrciæ*, U.S.P.), by distilling rum with leaves of *Myrcia acris*, etc., or by dissolving the oils in alcohol; and others.

Alcoholic drinks vary much in strength. Cider or apple-wine, perry or pear-wine, and good beer (ale and porter or stout) contain 4 to 6 per cent. of real alcohol; good light wines, both "red" and "white," and natural sherry also, 10 to 12 per cent.; strong sherry and port, which are commonly "fortified," that is contain added spirit, 16 or 18 per cent.; while "spirits" (gin, rum, brandy, whisky, etc.), and "liqueurs" (ratafia, almond-flavoured; maraschino, cherry-flavoured; curaçoa, orange-flavoured; chartreuse, a composite-flavoured liqueur, etc.), are "under-proof" or "over-proof," terms explained in a following paragraph. For excise purposes "beer" is any such liquid or substitute which contains more than 2 per cent. of proof spirit. The well-known effects of these spirituous fluids on the animal system would appear to be due primarily to alcohol, and secondarily to ethereal derivatives of alcohols. Some owe a part of their effect to non-volatile substances, for beer from which all alcohol, etc., has been removed by ebullition is said to have considerable effect on the human economy.

Spirit of French Wine (*Spiritus Vini Gallici*, B.P.), or *Brandy* is a coloured and flavoured variety of alcohol distilled from French wine. Its colour is that of light sherry, and is derived from the cask in which it has been kept, but is commonly deepened by the addition of burnt sugar. Its taste is due to the volatile flavouring constituents of the wine, often increased by the addition of artificial essences.

Varieties of Alcohol.—The weak spirit, concentrated by distillation till it contains 84 per cent. by weight of pure alcohol, is an ordinary article of trade; its specific gravity at 60° F. is 0·8382. This is common *Spirit of Wine*, the *Spiritus Rectificatus* of the British Pharmacopœia. The official *Proof Spirit** (*Spiritus Tenuior*, B.P.) contains 49¼ per cent. by weight, 57 by volume, of alcohol, and is made by diluting 100 volumes of "Rectified Spirit" with water until the well-stirred product measures 156 volumes. Sixty volumes of water will be required for this purpose, the liquids occupying less bulk after than before admixture. In the language of the Excise authorities, the rectified spirit of the Pharmacopœia would be described as "56 degrees over proof" (56 O.P.); that is, 100 volumes contain as much alcohol as is present in 156 volumes of proof spirit. Obviously, proof spirit may be made by diluting with water rectified spirit of any other strength than that mentioned above. Thus 100 fluid ounces of a spirit of "seventy over proof" may be diluted to 170, or the same quantity of a spirit of "fifty over proof" may be diluted to 150, and so on. The specific gravity of proof spirit at 60° F. is 0·920. Spirit 10 per cent. "under proof" contains as much alcohol as would be present in spirit formed of 90 volumes of proof spirit mixed with sufficient water to form 100 volumes. According to British law, gin is not "adulterated" with water if it is not weaker than 35 degrees under proof; nor brandy, whisky, or rum if they are not weaker than 25 degrees under proof.

Absolute or *Real Alcohol* (C_2H_5HO) (*Alcohol Ethylicum*, B.P.) may be prepared from spirit of wine by removing the water which the latter contains. This is accomplished, partially, by anhydrous carbonate of potassium, and finally and entirely by recently fused chloride of calcium. In operating on, say, one pint, 2 ounces of dried carbonate of potassium is placed in a bottle that can be well closed, and frequently shaken during two days with the spirit. Meanwhile put rather more than a pound of chloride of calcium into a covered crucible, and subject it to a red heat for half an hour; then pour the fused salt on to a clean stone slab, cover it quickly with an inverted porcelain dish, and when it has congealed, break it up into small fragments, and enclose it in a dry stoppered bottle. Put one pound of this fused chloride of calcium into a flask, pour over it the spirit decanted from the carbonate of potassium, and closing the mouth of the flask with a cork, shake them together and allow them to stand for twenty-four hours with repeated agitation. Then attaching a dry condenser closely connected with a receiver from which free access of air is excluded, and applying the flame of a lamp to the flask, distil about two fluid ounces, which should be returned to the flask, after which the distillation is to be continued until fifteen fluid ounces have been recovered. The foregoing details are those of the British Pharmacopœia. The product should be "colourless and free from empyreumatic odour. Specific gravity from 0·797 to 0·800, and therefore containing 1 or at most 2 per cent. of water. It is entirely volatilized by heat, is not rendered turbid when mixed with water, does not cause anhydrous sulphate of copper to assume a blue colour even after the two have been well shaken together." What little water remains may, if necessary, be removed by the cautious addition of a little metallic sodium. If five per cent. of sodium be used, solution of ethylate of sodium, or caustic alcohol results (*Liquor Sodii Ethylatis*, B.P.) by replacement of the hydroxyl hydrogen by sodium:—$Na_2 + 2C_2H_5OH = 2C_2H_5ONa + H_2$. The solution contains 19 per cent. of ethylate of sodium.

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* *Proof spirit* is so termed from the fact that in olden times a proof of its strength was supposed to be afforded by moistening a small quantity of gunpowder and setting light to the spirit; if it fired the powder, it was said to be "over-proof"; if not, "under-proof." The weakest spirit that would stand this test was what we should now describe as of sp. gr. 0·920.

Tests.—There are no specific tests for alcohol when mixed with complex matters. It is, however, easily isolated and concentrated by fractional distillation, and is then recognisable by conjoint physical and chemical characters. Thus its odour and taste are characteristic; it is lighter than water, volatile, colourless, and when tolerably strong, inflammable, burning with an almost non-luminous flame; it readily yields aldehyde (*see* below) and acetic ether (*vide* Index), each of which has a characteristic odour; and, in presence of hot acid, alcohol reduces red chromate of potassium to a green salt of chromium.

According to Lieben, 1 of alcohol in 2,000 of water can be detected by adding to some of the warmed liquid a little iodine, a few drops of solution of soda, again warming gently, and setting aside for a time; a yellowish crystalline deposit of *iodoform* (CHI_3) is obtained. Under the microscope the latter presents the appearance of hexagonal plates or six-rayed and other varieties of stellate crystals.

$$C_2H_6O + 4I_2 + 6NaHO = CHI_3 + NaCHO_2 + 5NaI + 5H_2O.$$

Other alcohols, aldehydes, gum, turpentine, sugar, and several other substances give a similar reaction.

Tests of Purity.—Oil or resin is precipitated on diluting spirit of wine with distilled water, giving an opalescent appearance to the mixture. The sp. gr. of rectified spirit is 0·838. Fusel oil, aldehyde, and such impurities are detected by nitrate of silver (*vide* Index, "Alcohol, Test for purity of"). Water in absolute alcohol may be detected by adding to a small quantity a little highly dried sulphate of copper, which becomes blue ($CuSO_4$, $5H_2O$) if water be present, but retains its yellowish-white anhydrous character ($CuSO_4$) if water be absent.

Note.—Most ethyl derivatives are formed from alcohol, such as the nitrite of ethyl in spirit of nitrous ether, iodoethane, etc. These have been treated under "Ethane." Aldehyde and acetic acid are obtained from alcohol by oxidation.

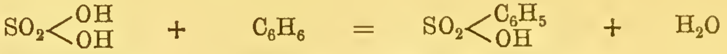
Alcohols and Ethers.—As already stated, just as such elementary radicals as potassium (K) form hydrates,—as KOH,—and oxides,—as K_2O,—so do such compound radicals as ethyl (C_2H_5) form hydrates,—as common alcohol, C_2H_5OH, and other alcohols, p. 520,—and oxides,—as common ether, $(C_2H_5)_2O$, and other ethers, p. 533.

But *Sulphur Alcohols*, or *Thio-alcohols*, CH_3SH, C_2H_5SH, etc., analogous to sulphydrates, KHS, etc., are known. They were originally termed *mercaptans* (*mercurius captans*) from the readiness with which they took mercury captive, $(C_2H_5S)_2Hg$. *Sulphur Ethers*, or *Thio-ethers*, also are known, $(CH_3)_2S$, $(C_2H_5)_2S$, etc. The vapours of such sulphur compounds have an extremely unpleasant smell.

Sulphonic Acids are products of the oxidation of the sulphur alcohols just mentioned. For example:—

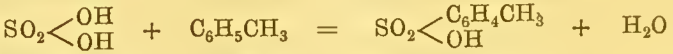
$$\underset{\text{Ethyl-mercaptan.}}{2C_2H_5SH} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Ethyl-sulphonic acid.}}{2C_2H_5{\cdot}SO_2{\cdot}OH}$$

They also may be formed by acting on hydrocarbons with sulphuric acid. Examples :—



$$\mathrm{SO_2}<^{\mathrm{OH}}_{\mathrm{OH}} + \mathrm{C_6H_6} = \mathrm{SO_2}<^{\mathrm{C_6H_5}}_{\mathrm{OH}} + \mathrm{H_2O}$$

Sulphuric acid. Benzene. Benzene-sulphonic acid. Water.

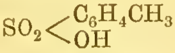


$$\mathrm{SO_2}<^{\mathrm{OH}}_{\mathrm{OH}} + \mathrm{C_6H_5CH_3} = \mathrm{SO_2}<^{\mathrm{C_6H_4CH_3}}_{\mathrm{OH}} + \mathrm{H_2O}$$

Sulphuric acid. Toluene. Toluene-sulphonic acid. Water.

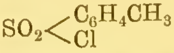
Sulphonic acids are isomeric with acid sulphites, the characteristic sulphonic group or radical being SO_3H, but the acid sulphites of the organic radicals are extremely unstable, the corresponding sulphonic acids very stable. *Orthophenolsulphonic acid*, $C_6H_4OH{\cdot}SO_2{\cdot}OH$, *sozolic acid*, or *aseptol*, is a non-poisonous, non-irritating antiseptic. The *di-iodo-paraphenolsulphonic acid*, or *sozoiodol*, $C_6H_2I_2OH{\cdot}SO_2{\cdot}OH$, has similar properties, and is used instead of iodoform.

Saccharin (*Glusidum*, B.P.; synonym, *Glucusimide*), which is a harmless, non-alimentary, purely sweetening agent, two or three hundred times as sweet as sugar, is *benzoyl-sulphonic imide.* Fahlberg obtains it by converting the toluene, $C_6H_5CH_3$, of coal tar into toluene-sulphonic acid (above); this into a calcium salt, then into a sodium salt, and the latter into toluone-sulphonic chloride, by action of trichloride of phosphorus and chlorine; the liquid ortho-chloride into amide by ammonium carbonate; the amide is then oxidised by potassium permanganate to sulphamidobenzoate and water; hydrochloric acid then precipitating benzoyl-sulphonic imide or "sacchariu" with elimination of water. "Soluble saccharin" is saccharin in which hydrogen is displaced by sodium. The following formulæ illustrate the stages of manufacture :—



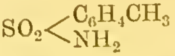
$$\mathrm{SO_2}<^{\mathrm{C_6H_4CH_3}}_{\mathrm{OH}}$$

Tolucnc-sulphonic acid.



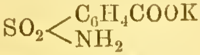
$$\mathrm{SO_2}<^{\mathrm{C_6H_4CH_3}}_{\mathrm{Cl}}$$

Toluenc-sulphonic chloride.



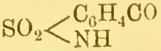
$$\mathrm{SO_2}<^{\mathrm{C_6H_4CH_3}}_{\mathrm{NH_2}}$$

Tolucno-sulphonic amide.



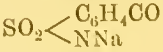
$$\mathrm{SO_2}<^{\mathrm{C_6H_4COOK}}_{\mathrm{NH_2}}$$

Sulphamidobenzoatc of potassium.



$$\mathrm{SO_2}<^{\mathrm{C_6H_4CO}}_{\mathrm{NH}}$$

Bonzoyl-sulphonic imido or "saccharin."



$$\mathrm{SO_2}<^{\mathrm{C_6H_4CO}}_{\mathrm{NNa}}$$

"Soluble saccharin."

Sulphonal (B.P.), a new hypnotic, is a crystalline, colourless, inodorous, tasteloss substanco; a product of the action of permanganate solution on morcaptol—a liquid resulting from the reaction of hydrochloric acid, mercaptan and acetone. Its descriptive name is diethylsulphon-dimethylmethane, and the following is its descriptive formula:—

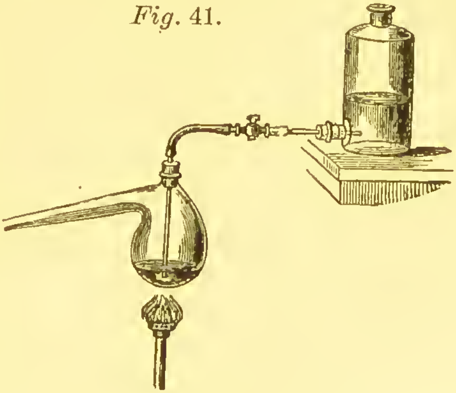
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C < \begin{matrix} SO_2C_2H_5 \\ SO_2C_2H_5 \end{matrix}$$

ETHERS.

Ethylic, or ordinary, Ether.—Into a capacious test-tube put a small quantity of spirit of wine and about half its bulk of sulphuric acid, mix, and gently warm; the vapour of ether, recognised by its odour, is evolved. Adapt a cork and long bent tube to the test-tube, and slowly distil over the ether into another test-tube. Half the original quantity of alcohol now placed in the generating-tube will again give ether; and this operation may be repeated many times.

On the larger scale, and according to the following official process (*Æther*, B.P.), the addition of alcohol, instead of being intermitting, is continuous, a tube conveying alcohol from a reservoir into the generating-vessel. Mix ten fluid ounces of sulphuric acid with twelve fluid ounces of rectified spirit in a glass retort or flask capable of containing at least two pints, and, not allowing the mixture to cool, connect the retort or flask, by means of a bent glass tube, with a Liebig's condenser, and distil with a heat sufficient to maintain the liquid in brisk ebullition. (If a thermometer also be inserted in the tubulure of the retort or through the cork of the flask, the temperature may be still more carefully regulated—between 284° and 290° F.) As soon as the ethereal fluid begins to pass over, supply fresh spirit in a continuous stream, and in

Fig. 41.



PREPARATION OF ETHER.

such quantity as to about equal the volume of the fluid which distils. For this purpose use a tube furnished with a stopcock to regulate the supply, as shown in fig. 41 above, connecting one end of the tube with a vessel containing the spirit supported above the level of the retort or flask, and passing the other end through the cork of the retort or flask into the liquid. When a total of fifty fluid ounces of spirit has been added, and forty-two fluid ounces of ether have distilled over, the process may be stopped.

To *partially purify* the liquid, dissolve ten ounces of chloride of calcium in thirteen ounces of water, add half an ounce of lime, and agitate the mixture in a bottle with the impure ether. Leave the mixture at rest for ten minutes, pour off the light supernatant fluid, and distil it with a gentle heat until a glass bead of specific gravity 0·735 placed in the receiver begins to float. The ether and spirit retained by the chloride of calcium and by the residue of each rectification may be recovered by distillation and used in a subsequent operation.

Explanation of Process.—On the addition of sulphuric acid to alcohol in equal volumes, one molecule of each react and give a molecule of ethylhydrogen sulphate and one of water:—

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethylhydrogen}\\\text{sulphate.}}}{C_2H_5HSO_4} + \underset{\text{Water.}}{H_2O.}$$

More alcohol then gives ether and sulphuric acid by the reaction of one molecule of the alcohol on one of ethylhydrogen sulphate (sometimes termed ethylsulphuric acid or sulphothylic acid, or sulphovinic acid):—

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5OH} + \underset{\substack{\text{Ethylhydrogen}\\\text{sulphate.}}}{C_2H_5HSO_4} = \underset{\substack{\text{Ether,}\\\text{or } C_2H_5-O-C_2H_5}}{(C_2H_5)_2O} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4.}$$

The water of the first reaction and the ether of the second distil over, while the sulphuric acid liberated is attacked by alcohol and reconverted into ethylhydrogen sulphate. So that the sulphuric acid originally employed finally remains in the retort in the form of ethylhydrogen sulphate. The effect, however, of a small quantity of sulphuric acid in thus converting a large quantity of alcohol into ether is limited, secondary reactions occurring to some extent after a time.

Mixed Ethers.—That $C_2H_5-O-C_2H_5$ represents the constitution of ether is indicated by the result of the reaction of, say, methylalcohol on ethylsulphuric acid, a single definite substance, methyl-ethyl ether $CH_3-O-C_2H_5$ resulting.

Ethers of various radicals, $R-O-R$, and several *mixed ethers*, R_a-O-R_b, and *sulphur ethers*, or *thio-ethers*, $R-S-R$, are known.

Properties.—Pure ethylic ether is gaseous at temperatures above 95° F.; hence the condensing-tubes employed in its distillation must be kept as cool as possible. At all ordinary temperatures it rapidly volatilizes, absorbing much heat from the surface on which it is placed. A few drops evaporated consecutively from the back of the hand produce great cold; and if blown in the form of spray, the cooling effect is so rapid and intense as to produce local anæsthesia. Evaporated by aid of a current of air from the outside of a thin narrow test-tube containing water, the latter is solidified to ice. Its vapour is very heavy, more than twice and a half as heavy as air, and nearly forty times as heavy as hydrogen ($H_2=2$; $C_4H_{10}O=74$; or as 1 to 37). In a still atmosphere it will flow a considerable distance along a table or floor before complete diffusion occurs. The vapour is highly inflammable; hence the importance of keeping candle and other flames at a distance during manipulations with ether. Exposed to the action of air and light, ether becomes charged with a little peroxide of hydrogen.

Purification.—To imitate the process of partial purification above described, add to the small quantity of ether obtained in the foregoing operation a strong solution of chloride of calcium and a little slaked lime; the latter absorbs any sulphurous acid that may have been produced by secondary decompositions, while the former absorbs water; on shaking the mixture and then setting aside for a minute or two, the ether will be found floating on the surface of the solution of chloride of calcium.

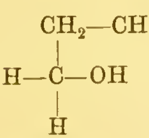
This ether, redistilled until the distillate has a sp. gr. not higher than 0·735, and boiling-point not higher than 105° F., is the ether of the British Pharmacopœia. It still contains about 8 per cent. of alcohol. The latter may be removed by well shaking the ether with half of its bulk of water, setting aside, separating the floating ether and again shaking it with water; alcohol is thus washed out. This washed ether containing water (for water and ether are to some extent soluble the one in the other; fifty measures of pure ether agitated with an equal volume of water are reduced to forty-five measures) is placed in a retort with solid chloride of calcium and a little caustic lime, and once more distilled; pure dry ether (*Æther Purus*, B.P.) results. Sp. gr. not exceeding 0·720, indicating about 99 per cent. of real ether. Shaken with about a fourth of its bulk of solution of iodide of potassium and a little starch mucilage, little or no blue colour is produced, indicating absence of an impurity. The exact nature of the latter is not known, but inasmuch as it develops peroxide of hydrogen, Dunstan and Dymond suggest that the test for the latter should always be applied. Poleck and Thummel state that the impurity in ether which causes potash to yield a brown colour is vinyl alcohol. On shaking pure ether with half its bulk of a dilute solution of bichromate of potassium acidified by sulphuric acid, and setting aside, the supernatant ether has no blue colour.

Spiritus Ætheris, B.P., is a mixture of common ether (*Æther*, B.P.) with twice its bulk of rectified spirit.

ALCOHOLS,—*continued.*

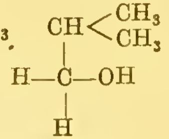
Propylic and Butylic Alcohols.

The primary and secondary propyl alcohols—$C_2H_5CH_2OH$ and $(CH_3)_2$ CHOH—and the four isomeric butyl alcohols (C_4H_9OH—see below) are of little pharmaceutical interest.



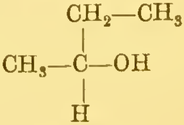
$$\begin{array}{l}\quad CH_2-CH_2-CH_3\\ \quad\;|\\ H-C-OH\\ \quad\;|\\ \quad\;H\end{array}$$

Primary
normal-butyl
alcohol.



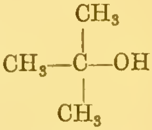
$$\begin{array}{l}\quad CH{<}^{CH_3}_{CH_3}\\ \quad\;|\\ H-C-OH\\ \quad\;|\\ \quad\;H\end{array}$$

Primary
iso-butyl
alcohol.



$$\begin{array}{l}\qquad\quad CH_2-CH_3\\ \qquad\quad|\\ CH_3-C-OH\\ \qquad\quad|\\ \qquad\quad H\end{array}$$

Secondary
butyl
alcohol.



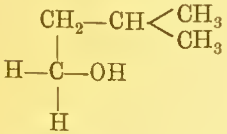
$$\begin{array}{l}\qquad\quad CH_3\\ \qquad\quad|\\ CH_3-C-OH\\ \qquad\quad|\\ \qquad\quad CH_3\end{array}$$

Tertiary
butyl
alcohol.

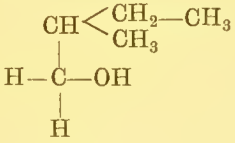
Amylic Alcohol.

Pentylic or Amylic Alcohol (*Fousel-oil*), (*Alcohol Amylicum* B.P.), ($C_5H_{11}HO$, or $C_4H_9CH_2OH$), is a constant accompaniment of ethylic or common alcohol (C_2H_5OH), especially when the latter is prepared from sugar which has been derived from starch; hence the name, from *amylum*, starch. The sugar of potato-starch yields a considerable quantity; hence the alcohol is often called *potato-oil.* It is also termed *fousel-oil* or *fusel oil* (from φύω, *phuo*, to produce), in allusion to the circumstance that the supposed oil is not simply educed from a substance already containing it, as is usually the case with oils, but is actually produced during the operation. It was described as oil probably because it resembled oil in not readily mixing with water; but it is soluble to some extent in water, and is a true spirit, homologous with spirit of wine. It often contains variable proportions of propylic, butylic, and carprylic alcohols. (*See* also VALERIANIC ACID.) When used for medicinal purposes, "it should be redistilled, and the product passing over at 262° to 270° F. (or about 128° to 132° C.) alone be collected for use."

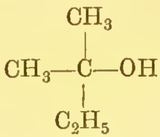
Amylic alcohol is "a colourless liquid, with a penetrating and oppressive odour and a burning taste. When pure, its specific gravity is ·818. Sparingly soluble in water, but soluble in all proportions in alcohol, ether, and essential oils. Exposed to the air in contact with platinum-black, it is slowly oxidized, yielding valerianic acid" ($C_4H_9{\cdot}COOH$). Two allotropic varieties of amylic alcohol exist, one, α, having no action on the other, β, lævo-rotating a polarized ray. The amylic alcohol of trade probably contains both varieties.



Primary
α, or inactive
amylic alcohol.



Primary
β, or active
amylic alcohol.



Tertiary
amylic alcohol.
"Amylene hydrate."

The constitution of the variety of amylic alcohol ($C_5H_{11}OH$), termed *tertiary amylic alcohol*, or *dimethyl-ethyl-carbinol*, is shown in the above graphic formula. It is used in medicine in place of chloral hydrate, and is known as amylene hydrate, for it contains the elements of amylene (C_5H_{10}) and water (H_2O).

The pentylic salts of pharmaceutical interest are all derived from amylic alcohol.

Other Monhydroxyl Alcohols.

Among the higher alcohols are the following:—

Cetylic Alcohol ($C_{16}H_{33}OH$), or *Hydrate of Cetyl*, formerly termed *ethal*, obtained by saponifying spermaceti (*Cetaceum*, B.P.), which consists of palmitate of cetyl ($C_{16}H_{33}C_{16}H_{31}O_2$), or *cetine*. Spermaceti is the solid crystalline fat accompanying sperm-oil in the head of the spermaceti whale.

Cerylic Alcohol ($C_{27}H_{55}OH$) is obtained in a similar manner from Chinese-wax (ceryl cerotate).

Melissic Alcohol ($C_{30}H_{61}OH$) is obtained in a similar manner from melissic palmitate, the portion of beeswax soluble in hot alcohol. *Yellow Wax* (*Cera Flava*, B.P.) and the same bleached by exposure to moisture, air, and sunlight, or White Wax (*Cera Alba*, B.P.) is the prepared honeycomb of the hive-bee. According to Brodie it is in the main a compound of the melissic ($C_{30}H_{61}$) and cerotic ($C_{26}H_{53}COO$) radicals with about five per cent. of *ceroleine*, the body to which the colour, odour, and tenacity of wax are due. Amongst the possible adulterants of wax are paraffin and *ceresine*. The latter is the purified native *ozokerite* of Galicia, a solid hydrocarbon, largely used as a substitute for beeswax, especially in Russia. Both paraffin and ceresine reduce the melting-point of wax, which should not be lower than 146° F. (63·3° C.) when taken in the manner described in connection with the quantitative determination of temperature (*vide* Index). The amount is obtained by destroying the wax with warm oil of vitriol, and afterwards with fuming sulphuric acid, which scarcely affects paraffin and ceresine. Pure wax will not yield more than about three per cent. to cold rectified spirit, whereas rosin, etc., would be extracted by the spirit. Solution of soda extracts nothing from pure wax, but dissolves fat acids, fats, rosin, Japan-wax, etc., and the alkaline fluid then yields a precipitate of acids on the addition of hydrochloric acid. Soap would be dissolved from wax on boiling the sample with water, and the aqueous fluid would yield oily acid on adding hydrochloric acid. Flour or any starch would be detected in the cooled aqueous fluid by iodine.

The Allylic Series of Alcohols ($C_nH_{2n-1}OH$) (monhydric alcohols).

Allylic alcohol ($C_3H_5{\cdot}OH$) may be obtained by heating 4 parts of glycerin with one of oxalic acid, the receiver being changed at 195° C., and the liquid collected till the temperature rises to 260° C. The first product is formic acid, which reacts on glycerine, forming monoformin:—

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Formic acid.}}{HCOOH} = OH_2 + \underset{\text{Monoformin.}}{C_3H_5(OH)_2(H\cdot COO)}.$$

This, on further heating, yields allylic alcohol:—

$$C_3H_5(OH)_2H\cdot COO = H_2O + CO_2 + C_3H_5OH.$$

By the action of the haloid acids it produces iodine, bromine, and chlorine derivatives, by replacing the OH by I, Br, or Cl; these derivatives, when digested with potassium sulphocyanate, yield allyl sulphocyanate or artificial *Oil of Mustard* (identical in composition with the chief constituent of the natural oil), the sulphocyanate of allyl being the body to which mustard owes its power of inducing inflammatory action on the skin (*Cataplasma Sinapis*, B.P.; and *Charta Sinapis*, B.P.).

Mustard (*Sinapis*, B.P.) is a powdered mixture of black or, rather, reddish-brown mustard-seeds (*Sinapis Nigræ Semina*, B.P.) from the *Brassica nigra*, and white mustard-seeds (*Sinapis Albæ Semina*, B.P.) from the *Brassica alba*. The white mustard-seed contains *sinalbin* ($C_{30}H_{44}N_2S_2O_{16}$), a glucoside which, in contact with the myrosin in an aqueous extract of mustard yields the sulphocyanate of the radical *acrinyl*, a body which forms part of the essential oil of mustard paste.

$$\underset{\text{Sinalbin.}}{C_{30}H_{44}N_2S_2O_{16}} = \underset{\substack{\text{Sulphocyanate}\\\text{of acrinyl.}}}{C_7H_7OCNS} + \underset{\substack{\text{Acid sulphate}\\\text{of sinapisine.}}}{C_{16}H_{24}O_5NSHSO_4} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

The black contains the albumenoid ferment, *myrosin*, resembling the *emulsin* of almonds and also myronate of potassium, or *sinigrin*. The latter is the body which, under the influence of the former, yields the chief part of the pungent oil of mustard paste. The amount of myrosin in black mustard is scarcely sufficient to decompose the whole of the sinigrin, while in white mustard the amount is more than sufficient to decompose the sinalbin. Hence the most effective mustard is a mixture of white and black.

The ferments act most effectively, hence the maximum amount of pungency is produced, in mustard paste at temperatures not exceeding 100° F. This temperature is contemplated in preparing *Cataplasma Sinapis*, B.P.

$KC_{10}H_{18}NS_2O_{10}$	$=$	$KHSO_4$	$+$	C_3H_5CNS	$+$	$C_6H_{12}O_6$
Myronate of potassium.		Acid sulphate of potassium.		Isosulphocyanate of allyl.		Glucose.

Crude oil of mustard often contains *cyanide of allyl*, C_3H_5CN.

In the Pharmacopœia of India the seed of *Brassica juncea*, *Rai*, or *Indian Mustard Plant*, is official in addition to that of *B. alba* and *B. nigra*. It is the common mustard of warm countries. It does not differ chemically from other mustard. Allyl compounds are also met with in several other cruciferous and liliaceous plants. *Oil of garlic* owes its odour to a sulphide of allyl $(C_3H_5)_2S$, some say to a "disulphide." The former may be artificially obtained by acting on allyl iodide by potassium sulphide:—

$2C_3H_5I$	$+$	K_2S	$=$	$(C_3H_5)_2S$	$+$	$2KI.$
Iodide of allyl.		Potassium sulphide.		Sulphide of allyl.		Iodide of potassium.

Decylene Alcohol, $C_{10}H_{19}OH$, belongs to this series. Menthol (*Menthol*, B.P.), obtained from oil of peppermint, is said by some to consist wholly of this alcohol.

QUESTIONS AND EXERCISES.

Give an outline of the relations between alcohols and acids.—Give a general method of preparing the primary alcohols of the ethylic series.—Name the source of methylic alcohol.—What is "methylated spirit"?—Describe the mode of detecting methylated spirit in a tincture.—How can artificial ethylic alcohol be prepared?—Write a few sentences on the formation, purification, and concentration of alcohol, and explain the difference between rectified spirit, proof spirit, and absolute alcohol.—What quantity of water must be added to one gallon of spirit of wine 56 degrees over proof, to convert it into proof spirit?—How far must 5 pints of spirit of wine of 53 degrees over proof be diluted to become proof spirit? *Ans.*, 7 pints 13 ounces.—State the specific gravity of proof spirit.—State the proportion of alcohol commonly present in malt liquors, light wines, port and sherry, and "spirits;" and state the extent to which spirits may be diluted without "adulteration."—Enumerate the characters of alcohol.—Whence is brandy obtained? and to what are due its colour and flavour?—Describe the official process for the preparation of ether, giving equations.—Offer a physical explanation of the mode of producing local anæsthesia.—How is commercial ether purified?—Is "amylic alcohol" a simple or a complex body?—How is allylic alcohol prepared? In what relation does allylic alcohol stand to oil of mustard and oil of garlic?

Alcohols of the $C_nH_{2n-7}OH$ *Series. Phenols and Benzylic Alcohols.* These are alcohols only in the sense of being hydroxyl derivatives of hydrocarbons. Unlike the paraffin alcohols, they do not yield aldehydes, oxidation acids, or ketones.

Carbolic Acid.

Phenol, *Phenic Alcohol*, *Phenic Acid*, or *Carbolic Acid*[*] (C_6H_5OH), may be artificially obtained by heating benzene with sulphuric acid, which forms benzene-sulphonic acid (p. 530), ($C_6H_5HSO_3$), this, when heated with potash, yielding the phenate or carbolate of potassium, and this, with acids, the phenol :—

$$\underset{\text{Benzene-sulphonic acid.}}{C_6H_5HSO_3} + \underset{\text{Potassium hydrate.}}{3KHO} = \underset{\text{Potassium carbolate.}}{C_6H_5OK} + \underset{\text{Sulphite of potassium.}}{K_2SO_3} + \underset{\text{Water.}}{2H_2O.}$$

Commercially, carbolic acid is obtained from that part of coal tar boiling between 180° and 190° C. When purified, it is a colourless[†] crystalline body (*Acidum Carbolicum*, B.P.). A crystalline, so-called hydrous, acid (C_6H_5OH,H_2O) may also be obtained.

At temperatures above 95° F. ordinary carbolic acid is an oily liquid. It is only slightly soluble in water, but readily dissolved by alcohol, ether, and glycerine (*Glycerinum Acidi Carbolici*, B.P.). At 60° F. (15·5° C.), 100 parts of the acid are liquefied by the addition of 5 to 10 parts of water (100 of acid and ten of water added forming the *Acidum Carbolicum Liquifactum*, B.P.); dissolve 30 to 40 of water, and are dissolved by 1,800 to 1,200 of water ; the former and latter of these numbers being respectively characteristic of the acicular and pulverulent varieties of the acid. In odour, taste, and solubility (and in appearance when liquefied by heat or by the addition of 5 per cent. of water) it resembles creasote, a wood-tar product for which carbolic acid has been substituted. Besides phenol (C_6H_5OH), coal-tar oil contains *cresol*, cresylic acid (C_7H_7OH), or ($C_6H_4CH_3OH$), the alcohol of toluene, while wood-tar oil furnishes *guaiacol* ($C_7H_8O_2$)—also a product of the destructive distillation of guaiacum-resin, boiling-point 200° C.—and *creasol* ($C_8H_{10}O_2$), or creasote. Certain colouring-matters may be obtained by the oxidation of carbolic acid: ammonia or, still better, phenyl-ammonia (aniline or phenylamine) mixed with it, and then a small quantity of solution of a hypochlorite, gives a blue liquid. No very satisfactory chemical method can be found for distinguishing creasote from carbolic acid, as creasote contains phenol, the chief difference consisting in the fact that the former boils only at 370° F., while the latter readily dries up at 212°. Some other physical differences exist: thus, carbolic acid does not affect a ray of polarized light; creasote twists it slightly to the right. Carbolic acid is either solid or may be solidified by cooling; creasote is not solidified by the cold produced by a mixture of hydrochloric acid and sulphate of sodium. Creasote from coal (impure or crude carbolic acid) gives a jelly when shaken with albumen or with collodion; creasote from wood (*Creasotum*, B.P.) is scarcely affected, especially if quite free from even all natural traces of carbolic acid. Coal-creasote is soluble in solution of potash and in the strongest solution of ammonia (Read), wood-creasote scarcely soluble. The coal product is soluble in twenty volumes of water, and a neutral solution of ferric chloride strikes a more or less permanent green or blue colour with the liquid; wood-creasote is less soluble (*Aqua Creosoti*, U.S.P., is said to contain 1 in 129) and not permanently coloured blue by ferric chloride. An alcoholic solution of the coal-oil is coloured brown by ferric chloride, a similar solution of true creasote green. A dilute solution of creasote, such as creasote water, is not affected by agitation with spirit of nitrous ether, while a similar solution of phenol becomes red. A few drops of the spirit of nitrous ether are placed in a test-tube, then about a drachm of the aqueous fluid, and an equal volume of sulphuric acid is poured down the sides of the tube. A pink or red colour results if phenol be present, especially after standing aside a short time (Eykman; MacEwan). A solution of carbolic acid gives, with excess of bromine water an insoluble white precipitate of tribromophenol, $C_6H_2Br_3OH$. This reaction is useful in quantitative estimations of carbolic acid. The extent of absorption of iodine by alkaline solutions of this and other phenols (thymol, naphthol, etc.) serves also for quantitative purposes. According to Morson pure creasote is unaffected when mixed with an equal volume of commercial glycerine, while carbolic acid is miscible in all proportions, and will carry into solution even a considerable quantity of creasote.

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[*] Ordinary carbolic acid is a mixture of phenol, cresol, and other homologues.

[†] Phenol soon assumes a pink colour owing (Fabrini) to the action of peroxide of hydrogen and ammonia in presence of traces of copper, iron, or lead.

Carbolic acid and alkalies yield *carbolates* or *phenylates*, as C_6H_5OK, C_6H_5ONa. Alcoholic solutions of the latter and of mercuric chloride yield yellow crystalline mercuric phenylate or *phenol-mercury* $(C_6H_5O)_2Hg$.

Carbolic acid is a powerful *antiseptic* (ἀντί, *anti*, against, and σήπω, *sēpō*, to putrefy). In large doses it is poisonous, *antidotes* being a mixture of olive-oil and castor-oil, freely administered, or a mixture of slaked lime, with about three times its weight of sugar rubbed together with a little water. Carbolic acid is soluble in sulphuric acid, *sulphocarbolic acid*, *phenol-sulphonic acid* $(C_6H_4(OH)SO_3H)$, or *sulphophenic acid*, being formed. On diluting and mixing with oxides, hydrates, or carbonates, *sulphocarbolates* are formed. The formula of *sulphocarbolate of sodium* is $NaC_6H_5SO_42H_2O$, or $C_6H_4(OH)SO_3Na, 2H_2O$. It is obtained by saturating sulphocarbolic acid by carbonate of barium, and decomposing the resulting soluble sulphocarbolate of barium, $(C_6H_4OHSO_3)_2Ba$, by carbonate of sodium until a precipitate of carbonate of barium ceases to form. The filtrate on evaporation yields colourless, neutral, prismatic crystals of the salt (*Sodii Sulphocarbolas*, B.P.), the old Sulphocarbolate of Soda. *Sulphocarbolate of Zinc*, $(C_6H_4OHSO_3)_2Zn, H_2O$ (*Zinci Sulphocarbolas*, B.P.), may be obtained by saturating sulphocarbolic acid with oxide of zinc.

Trinitro-phenol $(C_6H_2(NO_2)_3OH)$ is formed on slowly dropping carbolic acid into fuming nitric acid; it is the yellow dye known as *carbazotic acid*, or *picric acid*; most of the picrates are explosive by percussion.

Both carbolic acid and benzene are secondary products, obtained in the manufacture of coal-gas; hence, indeed, the word *phenic* and thence *phenyl* (from φαίνω, *phainō*, I light, an allusion to the use of coal-gas).

By heating phenol with zinc dust, benzene results,—

$$C_6H_5OH + Zn = ZnO + C_6H_6.$$

Salicylic acid is made from phenol (*vide* Salicylic Acid).

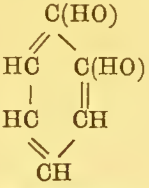
Constitution of Phenol—Phenol (C_6H_5OH) may be regarded as benzene (C_6H_6) in which one atom of hydrogen (H) is displaced by hydroxyl (OH). When two atoms of hydrogen in benzene are displaced by two of hydroxyl, *re-*

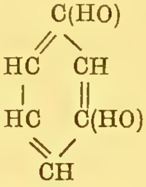
sorcin (C_6H_42OH) results, a colourless, crystalline antiseptic having many advantages over carbolic acid in surgical operations. Its name was given in allusion to its original source, resin, and to certain similarities with orcin. It occurs in white flat prisms readily soluble in most liquids. It may be made by passing benzol vapour into hot sulphuric acid and heating the product (benzenedisulphonic acid, $C_6H_4(SO_2{\cdot}OH)_2$) with excess of soda.

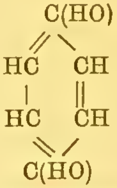
$$C_6H_4(SO_2{\cdot}NaO)_2 + 2NaHO = C_6H_4(OH)_2 + 2Na_2{\cdot}SO_3$$

Benzenedisulphonate of sodium.	Soda.	Resorcin.	Sulphite of sodium.

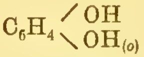
Ortho- Meta- and Para-Aromatic Compounds.—Resorcin is one of a group of three metameric dihydroxyl-benzenes. Their chemical relationships warrant the conclusion (on the atomic theory) that the cause of their differences in properties is a difference of position of the two atoms of hydroxyl in the molecule, these being, respectively, next to each other, separated by one atom (of CH), and by two atoms (of CH) (*see* Constitution of Benzene, p. 516), thus:—

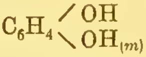

Ortho-dihydroxyl-benzene (pyrocatechin).

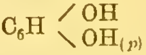

Meta-dihydroxyl-benzene (resorcin).


Para-dibydroxyl-benzene (hydroquinone).

The foregoing formulæ may conveniently be shortened as follows:—


$$C_6H_4\begin{matrix}/\,OH\\ \backslash\,OH_{(o)}\end{matrix}$$


$$C_6H_4\begin{matrix}/\,OH\\ \backslash\,OH_{(m)}\end{matrix}$$


$$C_6H\begin{matrix}/\,OH\\ \backslash\,OH_{(p)}\end{matrix}$$

In these formulæ the letters, *o*, *m*, or *p*, indicate the position of the atoms of hydroxyl (OH) in relation to each other; *o* signifying *the ortho position* of one atom in relation (next, or 1, 2) to the other; *m* signifying *the meta position* of one atom in relation (next but one, or 1, 3) to the other; and *p* signifying *the para position* of one atom in relation (next but two, or 1, 4) to the other. Among the benzene or aromatic compounds there are many such metameric trios (three xylenes, three phthalic acids, etc.), their occurrence strongly supporting "the benzene ring" hypothesis of Kekulé as to the constitution of benzene compounds.

Cresol or *Tolyl Alcohol*, $C_6H_4OH{\cdot}CH_3$, one of the alcohols of toluene, $C_6H_5CH_3$, is always found with crude phenol; artificially it may be made in the same manner as phenol, by acting on toluene with sulphuric acid and heating the resulting sulphonic acid ($C_6H_4(SO_3H)CH_3$) with potash. With ferric chloride it gives a brown coloration. The three forms, ortho-, meta-, para-, are known.

Benzylic Alcohol, Phenylcarbinol, $C_6H_5CH_2OH$, is isomeric with cresol, but has the hydroxyl group replaced in the methane nucleus, and not in the benzene nucleus of toluene. Having the CH_2OH group, on oxidation it yields benzoic aldehyde, C_6H_5COH (oil of bitter almonds), and benzoic acid, C_6H_5COOH.

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b. Dihydroxyl Derivatives of Hydrocarbons.

Dihydric, or *Dihydroxylic*, or *Diacid Alcohols.* Glycols. $C_nH_{2n}(OH)_2$ series (*see* also p. 488).—Glycols may be viewed as dihydroxyl derivatives of the paraffins, the alcohols of the ethylic series being mono-derivatives :—

C_2H_6	C_2H_5OH	$C_2H_4(OH)_2$
Ethane.	Ethyl alcohol.	Glycol.

They are prepared by acting on di-iodo-derivatives of the paraffins by acetate of silver, and then treating with potash.

$$\underset{\text{Di-iodoethane.}}{C_2H_4I_2} + \underset{\text{Acetate of silver.}}{2CH_3COOAg} = \underset{\text{Acetate of ethylene.}}{(CH_3COO)_2C_2H_4} + \underset{\text{Iodide of silver.}}{2AgI}$$

$$\underset{\text{Acetate of ethylene.}}{(CH_3CO{\cdot}O)_2C_2H_4} + \underset{\text{Potash.}}{2KHO} = \underset{\text{Glycol.}}{C_2H_4(OH)_2} + \underset{\text{Acetate of potassium.}}{2CH_3{\cdot}COOK}$$

The glycols yield very interesting results on oxidation, forming two sets of acids, the lactic and the succinic series.

Aromatic Glycols, $C_nH_{2n-8}(OH)_2$, *and Saligenin Alcohols.*—For the dihydric alcohols of benzene, namely, resorcin, pyrocatechin, and hydroquinone, *see* Phenol. *Toluene dihydric alcohols. Orcin*, $C_6H_3(OH)_2CH_3$. This is found in lichens. *Hydroxybenzylic alcohol*, salicylic alcohol, saligenol, saligenin, $C_6H_4OH \cdot CH_2OH$. This is obtained from the salicin of willow bark. Having the hydroxyl group in the methane nucleus as well as in the benzene nucleus, salicylic aldehyde ($C_6H_4OH \cdot COH$) and salicylic acid ($C_6H_4OH \cdot COOH$) are formed on oxidation.

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c. *Trihydroxyl Derivatives of Hydrocarbons.*

Trihydric Alcohols.—$C_nH_{2n-1}(OH)_3$ series. Glycerols.

Glycerine.

Glycerol,* propenyl alcohol, glycerine, $C_3H_5(OH)_3$.—The propenyl (glycyl or glyceryl) of glycerine in combination with many of the acidulous radicals of the acids, oleic, palmitic, stearic, etc., forms most of the solid fats and oils. When these latter substances are heated with metallic hydrates (even with water—hydrate of hydrogen—at a temperature of 500° to 600° F.), double decomposition occurs, oleate, palmitate, or stearate of the metal is formed, and glycerol (propenyl hydrate) is set free. Hence glycerine is a by-product in the manufacture of soap, hard candles, and lead plaster (*vide* Index).

Properties.—Glycerine is viscid when pure, specific gravity 1·28 (about 1·25, B.P.), has a sweet taste, and is soluble in water or alcohol in all proportions. It has remarkable powers as a solvent, is a valuable *antiseptic* even when diluted with 10 parts of water, and useful as an emollient. In vacuo it may be distilled unchanged, but under ordinary atmospheric pressure it is decomposed by heat, especially if distillation be attempted in a flask or retort. In a shallow open vessel heat readily vaporizes it if a little water be present. From damp air glycerine absorbs moisture slowly but in considerable proportions. Perfectly pure and anhydrous glycerine, at a few degrees below the freezing point of water, sometimes solidifies to a mass of crystals.

Tests.—Heat one or two drops of glycerine in a test-tube, alone or with strong sulphuric acid, acid sulphate of potassium, or other salt powerfully absorbent of water; vapours of acrolein, acrylic aldehyde (from *acer*, sharp, and *oleum*, oil) are evolved,—

---

* It will be noticed that all the alcohols have the termination *-ol*, carbinol, glycol, glycerol, saligenol, pyrogallol.

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Acrylic aldehyde.}}{CH_2CH \cdot COH}$$

recognised by their powerfully irritating effects on the eyes and respiratory passages. If the glycerine be in solution, the latter must be evaporated as low as possible before the test is applied.

To a little weak solution of borax, reddened by the addition of phenol-phthalein, add a few drops of the solution (neutralized, if necessary) suspected to contain glycerine; if any is present, the colour will be discharged owing to the liberation of free boric acid, but will re-appear on heating the solution; this reaction is also given by other poly-hydric alcohols, such as mannite or glucose.

Add a few drops of the fluid suspected to contain the glycerine to a little powdered borax; stir well together; dip the looped end of a platinum wire into the mixture, and expose to an air-gas flame; a deep green colour is produced (Senier and Lowe).

The glycerine liberates boric acid, which colours the flame (*see* p. 395). Ammoniacal salts, which similarly affect borax, must first be got rid of by boiling with solution of carbonate of sodium. Acids must also be neutralized. Liquids containing much indefinite organic matter must sometimes be evaporated to dryness, the residue extracted by alcohol, and the latter tested for the glycerine. To detect traces, liquids must be concentrated.

Glycerine, by action of very strong nitric acid, yields *nitro-glycerine*, or *nitrate of glyceryl* ($C_3H_53NO_3$). It is highly explosive, a very small quantity being liable to explode during preparation, and with great violence. 75 parts of nitroglycerine absorbed by 25 of porous silica, yield a pasty mass more convenient to handle than nitroglycerine itself; it is used for blasting, under the name of *dynamite*. Tablets of chocolate, weighing $2\frac{1}{2}$ grains, and containing $\frac{1}{100}$ grain of nitroglycerine, constitute the *Tabellæ Nitroglycerini*, B.P. A "one per cent." solution in rectified spirit (that is, 1 part by weight in 100 by volume) is the *Liquor Trinitrini*, B.P.; *Liquor Nitroglycerini*, B.P.; or *Liquor Glonoini*, B.P. Its specific gravity is 0·844.

Besides glycerine itself (*Glycerinum*, B.P.), there are several official preparations of glycerine,—solutions of carbolic, gallic, and tannic acids and borax in glycerine, and a sort of mucilage of starch in glycerine,—*Glycerinum Acidi Carbolici*, *Glycerinum Acidi Gallici*, *Glycerinum Acidi Tannici*, *Glycerinum Aluminis*, *Glycerinum Amyli*, *Glycerinum Boracis*, *Glycerinum Plumbi Subacetatis*, and *Glycerinum Tragacanthæ.*

FATTY BODIES.

Processes of extraction.—Fixed oils and fats are extracted from animal and vegetable substances by pressure or straining, with or without the aid of heat, or by digestion in solvents, as ether, etc., and evaporation of the solvent.

Constitution and general relations.—Fixed oils and fats are, apparently, almost as simple in constitution as ordinary inorganic salts. Just as acetate of potassium ($KC_2H_3O_2$) is regarded as a compound of potassium (K) with the characteristic elements of all acetates ($C_2H_3O_2$), so soft soap is considered to be a compound of potassium (K) with the elements characteristic of all oleates ($C_{18}H_{33}O_2$), and hence is chemically termed oleate of potassium ($KC_{18}H_{33}O_2$). Olive oil (*Oleum Olivæ*, B.P.), from which soap is officially prepared, is mainly oleate of the trivalent radical *glyceryl* (C_3H_5), the formula of such a fluid oil being $C_3H_53C_{18}H_{33}O_2$, and its name *oleine*. The formation of a soap therefore, on bringing together oil and a moist oxide or hydrate, is a simple case of double decomposition (or, rather, metathesis), as seen already in connection with lead plaster (p. 244), or in the following equation relating to the formation of common hard soap :—

$$\underset{\substack{\text{Hydrate of sodium}\\ \text{(caustic soda).}}}{3NaHO} + \underset{\substack{\text{Oleate of glyceryl}\\ \text{(vegetable oil).}}}{C_3H_53C_{18}H_{33}O_2} = \underset{\substack{\text{Oleate of sodium}\\ \text{(hard soap).}}}{3NaC_{18}H_{33}O_2} + \underset{\substack{\text{Hydrate of glyceryl}\\ \text{(glycerine).}}}{C_3H_53HO}$$

Berthelot has succeeded in preparing oil artificially from the oleate of hydrogen, or oleic acid, $HC_{18}H_{33}O_2$, and glycerine; and it is said to be identical with the pure oleine of olive oil and of other fixed oils.

Olive oil is liable to contain cotton-seed oil. The admixture may be detected by Bechi's test. Take 1 grain of crystallized nitrate of silver and dissolve it in the smallest possible quantity of water (about 1 c.c.), and add 200 c.c. of alcohol

(96°). The addition also of 20 c.c. of sulphuric ether is a good one, in that it makes the reagent better miscible with the oil to be examined, but it is not necessary. On the other hand prepare a solution composed of 85 parts of amylic alcohol and 15 parts of oil of rape seed. These reagents should be made as needed, and not kept on hand for any length of time. To apply the test, take 10 c.c. of the oil to be examined, add 1 c.c. of the alcoholic solution of nitrate of silver, and then from 8 to 10 c.c. of the mixture of amylic alcohol and oil of rape; agitating strongly and then heating on a water-bath for five or ten minutes. In the case of pure oils, the colour remains the same as it was after the addition of the reagents. If cotton-seed oil be present there will be produced a brownish colour, or turbidity, of a varying grade, from a very light brown to a deep maroon or black, according to the quantity of cotton oil present.

Hard fats chiefly consist of *stearine*—that is, of tristearate of glyceryl ($C_3H_5 3C_{18}H_{35}O_2$). Mr. Wilson, of Price's Candle Company, obtains stearic and oleic acids and glycerine by simply passing steam, heated to 500° or 600° F., through melted fat. Both the glycerine and fat-acids distil over in the current of steam, the glycerine dissolving in the condensed water, the fat-acids floating on the aqueous liquid. From oleate of glyceryl and hydrate of hydrogen there result oleate of hydrogen and hydrate of glyceryl.[*] The oleic acid (*Acidum Oleicum*, B.P.) is separated by cooling and pressing the mixture. It is "a straw-coloured liquid, nearly odourless and tasteless, and with not more than a very faint acid reaction. Unduly exposed to air, it becomes brown and decidedly acid. Specific gravity, 0·860 to 0·890. It is insoluble in water, but readily soluble in alcohol, chloroform, and ether. At 40° to 41° F. (4·5° to 5° C.) it becomes semi-solid, melting again at 56° to 60° F. (13·3° to 15·5° C.). It should be completely saponified when warmed with carbonate of potassium; and an aqueous solution of this salt, neutralized by acetic acid and treated with acetate of lead, should yield a precipitate which, after washing with boiling water, is almost entirely soluble in ether," showing the absence of any important quantity of stearic and palmitic acids, the lead stearate and palmitate being insoluble in ether.

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[*] Any such decomposition of water and fixation of its elements, whether direct as above, or indirect through the intermediate agency of saponification, is termed *hydrolysis* (ὕδωρ, *hudōr*, water, λύω, *lūo*, to decompose). The fixation of water without decomposition is termed *hydration*.

In a mixture of oils or fats and free fatty acids, tho latter may be estimated by taking advantage of their solubility in spirit of wine, and the formation of a neutral soap on shaking the spirituous solution with caustic soda, phenolphthaleïn being used as indicator. (*See* the section on the use of the caustic soda solution in volumetric analysis.)

The author found, *Pharmaceutical Journal*, March, 1863, that oleic acid readily combines with alkaloids and most of the metallic oxides or hydrates, forming *oleates* which are soluble in fats. In this way active medicines may be administered internally in conjunction with oils, or externally in the form of ointments (*Oleatum Hydrargyri*, B.P., and *Oleatum Zinci*, B.P.; *Oleatum Veratrinæ*, U.S.P.). Tichborne considers the formula of mercuric oleate to be $Hg(C_{18}H_{33}O_2)_2H_2O$.

Some fats, such as "suint" from sheep's wool, and the unctuous matter from bristles, feathers, horn and hair generally, yield, by saponification, etc., fatty acids and, instead of glycerine, *cholesterin*, an alcoholoid crystalline substance. The "lanolin" of pharmacy is cholesterin fat which has absorbed a large volume of water.

Adeps Lanæ, or Wool Fat, B.P., is "the purified cholesterin fat of sheep's wool." It is "a yellowish tenacious unctuous substance; almost inodorous; with a melting-point varying from 100° F. (37°·8 C.) to 112° F. (44°·4 C.); readily soluble in ether and in chloroform, sparingly soluble in rectified spirit. Ten grains should dissolve almost completely in fourteen fluid drachms of boiling ethylic alcohol, the greater part separating in flocks on cooling. Ignitod with free access of air, it burns, leaving but a trace of ash. Fifty grains dissolved in four fluid drachms of ether, and two drops of tincture of phenolphthaleïn added, should not require more than two grain-measures of volumetric solution of soda to produco a permanent red coloration. The solution in chloroform poured gently over the surfaco of sulphuric acid acquires a purplo-red colour. Heated with solution of soda, no ammoniacal odour should be evolved."

Adeps Lanæ Hydrosus, or Hydrous Wool Fat, B.P., is an intimate mixture of 7 parts of wool fat with 3 of water. It is commonly known as "Lanoline." It is "yellowish white; free from rancid odour. When hoated it separates into an upper oily and lower aqueous layer. One hundred grains exposed over a water-bath until the weight is constant yields not less than seventy grains, which should answer to the tests for wool fat."

Soaps.

Olive oil boiled with solution of potash yields potassium soap, or *soft soap* (*Sapo Mollis*, B.P.); with soda, sodium soap, or *hard soap* (*Sapo Durus*, B.P.), or *white Castile soap*, as distinguished from the variety of hard Castile, or Marseilles soap, which is "mottled" by iron soap; mixed with ammonia, an ammonium soap (*Linimentum Ammoniæ*, B.P.); and with lime-water, calcium soap (*Linimentum Calcis*, B.P.), —all oleates, chiefly, of the respective basylous radicals. Their mode of formation is indicated in the equation on page 546. The alkali soaps are soluble in alcohol, the others insoluble. A green soap, much used on the continent of Europe, and, indeed, official in Germany (formerly as *Sapo Viridis*, now as *Sapo Kalinus Venalis*), is made by adding indigo to ordinary soft soap; the yellow colour of the soap yielding with the indigo a greenish compound. The official characters of Hard Soap are :—"greyish-white, dry, inodorous; horny and pulverizable when kept in dry warm air; easily moulded when heated; soluble in rectified spirit; not imparting an oily stain to paper; incinerated it yields an ash which does not deliquesce." And of Soft Soap :—"yellowish-green, inodorous, of a gelatinous consistence; soluble in rectified spirit; not imparting an oily stain to paper: incinerated it yields an ash which is very deliquescent." Curd Soap (*Sapo Animalis*, B.P.) is "a soap made with soda and a purified animal fat, consisting principally of stearine." It will, of course, chiefly contain stearate of sodium. In pharmacy it is often advantageously employed instead of the "hard soap."

The hard soap met with in trade is made from all varieties of oil, the commoner kinds being simply the product of the evaporated mixture of oil and alkali, while the better sorts have been separated from alkaline impurities and the glycerine by the addition of common salt, or excess of lye, to the liquors, which causes the precipitation of the pure soap as a curd. Potash soap is not so readily precipitable by salt; moreover, some soda soap results. Saponification on the small scale is much facilitated by first well mixing the oil with 5 per cent. of sulphuric acid, and letting this mixture stand for twenty-four hours. The dark product is then readily soluble when boiled with soda, and the clear fluid yields a crust of white soap on cooling. If required quite free from alkali, the resulting soap is boiled with water until dissolved, salt added, and the whole cooled. A cake of pure soap results.

Yellow soap is a common, cheap soap, containing a good deal of resin soap, resin consisting chiefly of acids—pinic, sylvic, pimaric, etc.—which readily unite with alkalies to form true soaps.

Saponification.—This term is now extended in chemistry so as to include any process analogous to the foregoing,—any reaction in which an alkali decomposes any ethereal salt or alkyl salt.

Solid Fats.

1. *Lard* (*Adeps Præparatus*, B.P.) is the purified internal fat of the abdomen of the hog—the perfectly fresh *omentum* or *flare*, freely exposed to the air to dissipate animal odour, rubbed to break up the membranous vesicles, melted at about 130° F. (54·4° C.), and filtered through paper or flannel. 2. *Benzoated Lard* (*Adeps Benzoatus*, B.P.) is prepared lard heated over a water-bath with benzoin (one part to fifty), which communicates an agreeable odour and prevents or retards rancidity. Purified lard is a mixture of oleine (*lard oil*, removable by pressure) and stearine. *Margarine*, formerly supposed to be a constituent of lard and other soft fats, is now regarded as a mere mixture of *palmitine* (the chief fat of palm-oil) and stearine. 3. *Suet*, the internal fat of the abdomen of the sheep, purified by melting and straining, forms the official *Prepared Suet* (*Sevum Præparatum*, B.P.); it is almost exclusively composed of stearine ($C_3H_53C_{18}H_{35}O_2$). 4. Expressed oil of *Nutmeg* (*Oleum Myristicæ Expressum*, B.P.), commonly but erroneously termed *Oil of Mace*, is a mixture of a little volatile oil with much yellow and white fat; the latter is *myristin* or myristate of glyceryl ($C_3H_53C_{14}H_{27}O_2$). 5. Oil of *Theobroma*, or *Cacao butter* (*Oleum Theobromatis*, B.P.), chiefly stearine, but with one higher and some lower homologues (Heintz), is a solid product of the roasted and crushed seeds or *cocoa nibs* of the *Theobroma Cacao*. They contain from one-half to two-thirds of this fat. [Cocoa is too rich for use as food, hence is diluted with farina (*cheap cocoa*) or sugar (*chocolate*) or has a portion of its fat extracted,

while its solubility is, in one brand, usefully increased by a slight addition to its potassium.] 6. *Cocoa-nut* oil or butter, a soft fat contained in the edible portion of the nut of *Cocos nucifera*, or cocoa-nut of the shops, is a body containing glyceryl united with six acidulous radicals, namely, the caproic ($C_6H_{11}O_2$), caprylic ($C_8H_{15}O_2$), rutic ($C_{10}H_{19}O_2$), lauric ($C_{12}H_{23}O_2$), myristic ($C_{14}H_{27}O_2$), and palmitic ($C_{16}H_{31}O_2$)—radicals which, like some from resin, when united with sodium, form a soap differing from ordinary hard soap (oleate of sodium) by being tolerably soluble in a solution of chloride of sodium; hence the use of cocoa-nut oil and resin in making *marine soap*, a soap which, for the reason just indicated, readily yields a lather in sea-water. 7. *Kokum Butter*, Garcinia Oil, or Concrete Oil of Mangosteen, a whitish or yellowish-white fat obtained from the seeds of *Garcinia Indica* or *G. purpurea*, is composed of stearine, myristicine, and oleine. It is recognised officially in the Pharmacopœia of India (*Garciniæ purpureæ Oleum*).

Butter commonly yields 87½ per cent. of insoluble fat acids by saponification and decomposition of the soap by acid. Other animal fats, with which butter is likely to be adulterated, yield about 95½. Hence the percentage of fat acids, and, especially, volatile acids, insoluble acids, and soluble acids, yielded by a suspected sample of butter, indicates purity or the opposite. Occasionally, however, a sample of genuine butter may not conform to the figures, hence they cannot be relied on to show the exact extent of sophistication.

Fixed Oils.

Fixed and Volatile oils are naturally distinguished by their behaviour when heated; they also generally differ in chemical constitution—a fixed oil being, apparently, a combination of a basylous with an acidulous radical, as already stated, while a volatile oil is more commonly a neutral or normal hydrocarbon, mixed with a comparatively small proportion of a body—containing oxygen as well as carbon and hydrogen—to which the odour of the oil is generally due. The latter bodies are now articles of trade under the name of "concentrated essential oils."

Drying and Non-drying Oils.—Among fixed oils, most of which are oleate with a little palmitate and stearate of glyceryl, a few, such as—1. *Linseed Oil* (*Oleum Lini*, B.P., contained in *Lini Semina*, B.P., the ground residue of which is *linseed meal*, *Lini Farina*, B.P.), and, 2. *Cod-liver oil* (*Oleum Morrhuæ*, B.P.), and, to some extent, *castor* and *croton*, are known as *drying oils*, from the readiness with which they absorb oxygen and become hardened to a resin. Linseed commonly contains 37 or 38 per cent. of oil; 25 to 27 per cent. is obtained by submitting the ground seeds to hydraulic pressure, 10 to 12 per cent. remaining in the residual *oil-cake*. *Boiled oil* is linseed oil which has been boiled with oxide of lead. This treatment increases the already great tendency of linseed oil to resinify, forming *linoxyn* ($C_{32}H_{54}O_{11}$) on exposure to air. The drying oils appear to contain linoleine, an oily body distinct from oleine. Cod-liver oil contains an unimportant trace of iodine, 1 in one or two million parts, according to Stanford; a little choline also, and other bases, Gautier and Mourgues having recently isolated *aselline*, $C_{25}H_{32}N_4$, and *morrhuine*, $C_{19}H_{27}N_3$, besides butyl-, amyl-, and hexyl-amines and dihydro-lutidine. Among the *non-drying oils* are the following:—3. *Almond* oil (*Oleum Amygdalæ*, B.P.), indifferently yielded by the bitter (*Amygdala Amara*, B.P.) or sweet seed (*Amygdala Dulcis*, B.P.), to the extent of 45 and 50 per cent. respectively. 4. *Croton* oil (*Oleum Crotonis*, B.P.). Geuther states that no such acid as crotonic is obtainable from croton oil, but acetic, butyric, valerianic, and higher members of the oleic series, together with *tiglic acid*, $HC_5H_7O_2$. H. Senier states that alcohol separates croton oil into a soluble oil containing the powerful vesicating principle of croton oil and an insoluble non-vesicating but powerfully purgative principle. Kobert states that free crotonoleic acid is both the vesicant and the purgative. 5. *Lycopodium*, a yellow powder composed of the spores of the common Club-Moss (*Lycopodium clavatum*), contains a large proportion of a very fluid fixed oil; also an alkaloid (Bödeker) $C_{32}H_{52}N_2O_3$. 6. *Olive* oil (*Oleum Olivæ*, B.P.), already noticed. 7. *Castor* oil (*Oleum Ricini*, B.P.) chiefly a *ricinoleate of glyceryl* ($C_3H_5 3C_{18}H_{33}O_3$) or ricinoleine, a slightly oxidized oleine, soluble, unlike most fixed oils, in alcohol and in glacial acetic acid. Castor-oil seeds were stated, by Tuson, to contain an alkaloid, *ricinine*. Beck has recently confirmed Tuson, giving as the formula $C_{24}H_{32}N_7O_3$. It possesses no purgative property. They also contain an albumose, *ricin*, resembling, physiologically, but not quite chemically, the *abrin* of jequirity. 8. Oil of *male fern* (*Filix Mas*, B.P.); a vermifuge obtained by exhausting the rhizome with ether and removing the ether by evaporation—a dark-coloured oil containing a little volatile oil and resin, and officially termed an extract (*Extractum Filicis Liquidum*, B.P.). Its chief active constituent appears to be *filicic acid*, $C_{35}H_{42}O_{13}$. 9. Fixed oil of *mustard*, a bland, inodorous, yellow or amber oil, yielding by saponification and action of sulphuric acid, glycerine, oleic acid, and *erucic acid* ($HC_{22}H_{41}O_2$) (Darby). 10. *Arachis* oil (*Oleum Arachis*, P.I.) is found to the extent of 40 or 50 per cent. in the seeds of the *Arachis hypogæa* (P.I.), the Ground-nut or Earth-nut (so-called because the pod of the herb in the growth of its stalk downwards is forced beneath the surface of the ground and there ripens). It is chiefly oleine, but contains hypogæine, palmitine, and arachine. The oil is largely used in India in the place of olive oil, and is becoming much employed in Europe, especially for soap-making. 11. *Sesamé* oil (Gingelly, Teal, or Benne Oil) from the seeds of *Sesamum Indicum*, is also largely used in Europe. It has most of the characters of the best olive oil. It may be detected in olive oil by shaking the sample with a solution of pyrogallic acid in strong hydrochloric acid, and separating and boiling the acid fluid, a purplish colour resulting if sesamé be present. 12. *Shark-liver* oil, from *Squalus carcharias* (*Oleum Squalæ*, P.I.), is used as a substitute for cod-liver oil in India.

Trihydric Alcohols of the $C_nH_{2n-9}(OH)_3$ series.

Pyrogallol or *Pyrogallic acid.*—Trihydroxybenzene, $C_6H_3(OH)_3$. (*Vide* Index.)

d. Other polyhydroxyl Derivatives of Hydrocarbons.

Only one *tetrahydric alcohol* is known, namely *Erythrite*, or *Lichen Sugar*, $C_4H_6(OH)_4$, found in *Protococcus vulgaris*, *Roccella tinctoria*, and *R. fuciformis*. *Quercite*, the sugar of acorns, is *penthydric*; *Mannite* is *hexahydric*. *Sorbite* occurs in the fruits of the order *rosaceæ*.

Hexahydric Alcohols. *Mannite*, $C_6H_8(OH)_6$.—Boil manna with 15 or 16 parts of alcohol, filter, and set aside; mannite separates in colourless shining crystals or acicular masses, to the extent of from 60 to 80 per cent. of the manna. It is closely related to the ordinary sugars, glucose becoming mannite by action of nascent hydrogen:—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Mannite.}}{C_6H_{14}O_6}$$

Mannite does not undergo fermentation in contact with yeast. With nitric acid it forms explosive *nitromannite*, $C_6H_8(NO_3)_6$.

Manna, B.P., is "a concrete saccharine exudation obtained by making transverse incisions in the stems of cultivated trees of *Fraxinus Ornus.*" It occurs "in stalactitic pieces, varying in length and thickness, flattened or somewhat concave on their inner surface, and of a pale yellowish-brown colour, and nearly white externally. This manna, which is known as flake manna, is crisp, brittle, porous, crystalline in structure, and readily soluble in about six parts of water. Odour faint, resembling honey; taste sweet and honey-like, combined with a slight acridity and bitterness." It contains about 10 per cent. of moisture. Mannite is also met with in celery, onions, asparagus, certain fungi and sea-weeds, occurs in the exudations of apple- and pear-trees, and is produced during the viscous fermentation of sugar.

Dulcite, isomeric with mannite, is formed by the action of nascent hydrogen on inverted milk sugar. It differs from mannite by oxidizing to mucic acid, $C_6H_{10}O_8$, when treated with nitric acid.

QUESTIONS AND EXERCISES.

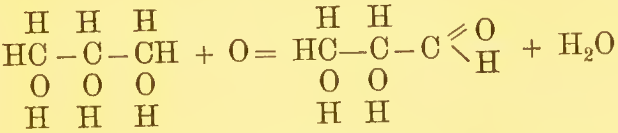
How is phenol artificially and commercially prepared?—How would you distinguish carbolic acid from creasote?—Give the formulæ and systematic names for picric acid, carbolate of sodium, and resorcin. Give names for the bodies having the formulæ $C_6H_4OH{\cdot}CH_3$ and $C_6H_5CH_2OH$.—What are glycols? how prepared?—Give formula and mention the chief properties of glycerine.—What is the specific gravity of glycerine?—By what test is glycerine recognised?—Enumerate some official preparations in which glycerine is employed.—Give a sketch of the general chemistry of fixed oils, fats, and soaps.—What is the difference between hard and soft soap?—Which soaps are official?—Name the source of lard. How is "Prepared Lard" obtained?—Mention the chief constituent of suet.—Whence is cacao-butter obtained?—Why is *marine soap* so called? and from what fatty matter is it almost exclusively prepared?—What do you understand by *drying* and *non-drying* oils?—In what respect does castor oil differ from other oils?—How is oil of male fern (*Ex. Filicis Liquidum*) prepared?—Classify pyrogallol (*Pyrogallic acid*), erythrite, mannite, and dulcite.—Describe the source and characters of manna.

CARBOHYDRATES.

Under the name *carbohydrates* have been grouped a large number of compounds containing carbon with hydrogen and oxygen in the same proportion as in water, and whose constitution has only recently been understood. They include sugars, dextrin, starch, cellulose, etc. The molecules of some of the latter are very complex, but are resolved by hydrolysis into sugars such as glucose.

The most commonly occurring carbohydrates contain six carbon atoms or even multiples of that number; but analogous bodies with three, five, seven or nine carbon atoms in the molecule have lately been discovered.

The sugars are the simplest of the carbohydrates in constitution, and a large number of them, some identical with previously known natural sugars, some previously unknown, have been synthesized. They are partially oxidized polyhydric alcohols, having one of their alcohol groupings oxidized into an aldehyde or ketone group. For example, the trihydric alcohol glycerine, on gentle oxidation with bromine, yields a body, *glycerose*, having all the characters of a sugar.



$$\underset{\substack{O\\H}}{\overset{H}{HC}}-\underset{\substack{O\\H}}{\overset{H}{C}}-\underset{\substack{O\\H}}{\overset{H}{CH}}+O=\underset{\substack{O\\H}}{\overset{H}{HC}}-\underset{\substack{O\\H}}{\overset{H}{C}}-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}+H_2O$$

This, however, is not stable, but spontaneously condenses into a glucose $C_6H_{12}O_6$.

Erythrose, $C_4H_8O_4$, is an example of a sugar with four, and *arabinose*, $C_5H_{10}O_5$, of one with five atoms of carbon. Most of the natural sugars are glucoses ($C_6H_{12}O_6$) or compounds of two or three molecules of glucoses minus water (*bioses* or *trioses*).

Sugars with seven, eight and nine atoms of carbon have been constructed by treating glucoses with hydrocyanic acid, which combines with the aldehyde or ketone group to form the nitrile of an acid containing one more carbon atom. This on hydrolysis gives the acid, the lactone of which may be reduced to the corresponding sugar by the action of nascent hydrogen. This process is then repeated to get an eight-carbon sugar, and so on. One of these seven-carbon sugars was found to be identical with a natural sugar, *perseite*, but most of them have not yet been found occurring naturally.

Glucoses, $C_6H_{12}O_6$.

Glucoses, $C_6H_{12}O_6$. There are two chief types of these six-carbon sugars differing from each other in the position of the alcohol grouping that has undergone oxidation, and classed accordingly as aldehyde and ketone sugars—*aldose* and *ketose*. *Dextrose* is an example of the first, and *lævulose* or *fructose* of the second class. Each of these classes contains a very large number of physical isomers, differing from each other in their action on polarized light and in some other respects; these may be most readily distinguished from one another by means of the physical characters of the compounds they form with phenyl-hydrazine (*see* Index). The large number of these isomers is accounted for, on the stereo-chemical theory, by the circumstance of there being no less than four asymmetrical carbon atoms in each molecule. Thus there are three dextroses, dextro-rotatory, lævo-rotatory, and inactive; three analogous mannoses; three fructoses or lævuloses, etc. Ordinary lævulose, or better fructose, is not therefore the mere optical isomer of dextrose, each of them having dextro-, lævo-, and inactive forms.

All the glucoses above mentioned have been obtained artificially, the starting-point being an artificial glucose (or *acrose*, $C_6H_{12}O_6$) obtained by the condensation of formic aldehyde, CH_2O ($6CH_2O = C_6H_{12}O_6$); it is probably in a similar way that natural sugars are produced by plants.

Dextrose, or *Grape-sugar*, or *Glucose* (from γλυκὺς, *glucūs*, sweet) is often seen in the crystallized state in dried grapes or raisins and other fruits; it is also the variety of sugar met with in diabetic urine. Its crystalline character is quite distinct from that of cane-sugar, the latter forming large four- or six-sided rhomboidal prisms, while grape-sugar occurs in masses of small cubes or square plates. Grape-sugar is also less soluble in water, but more soluble in alcohol than cane-sugar.

According to Fresenius, the percentage proportion of saccharine matter in the dried fig is 60 to 70, grape 10 to 20, cherry 11, mulberry 9, currant 6, whortleberry 6, strawberry 6, raspberry 4.

Fructose or *lævulose* is lævogyrate, while sucrose and glucose possess right-handed rotation; the latter twist a ray of polarized light from left to right, to an extent dependent on the amount of sugar present—a fact easy of application in estimating the amount of sugar in syrups or in diabetic urine.

Fructose or *lævulose* is the uncrystallizable, or very difficultly crystallizable, constituent of inverted cane-sugar. It is found in the grape, fig (*Ficus*, B.P.) cherry, gooseberry, strawberry, peach, plum and other fruits, often with dextrose or with cane-sugar. Fruit-sugar reduces cupric salts and ammonio-nitrate of silver.

Artificial formation of Grape-sugar from Cane-sugar. Tests for sugar.—Dissolve a grain or two of common cane-sugar in water. To a portion of this solution placed in a test-tube add more water, two or three drops of solution of sulphate of copper, a considerable quantity of solution of potash or soda (enough to turn the colour of the liquid from a light to a dark blue), and heat the mixture to the boiling-point; no obvious immediate change occurs. To another portion of the syrup add a drop of sulphuric acid, and boil for ten or twenty minutes, then add the copper solution and alkali, and heat as before; a yellowish-red precipitate of cuprous oxide (Cu_2O) falls. This test is exceedingly delicate.

The above reaction is due to the conversion of the *cane-sugar* ($C_{12}H_{22}O_{11}$) into *inverted sugar*—or *lævulose*, $C_6H_{12}O_6$ (so called because its solution causes left-handed rotation of a ray of polarized light, cane-sugar having an opposite effect) and *grape-sugar*, $C_6H_{12}O_6$, H_2O— by the influence of the sulphuric acid, and to the reducing action of the lævulose and grape-sugar on the cupric solution. The formation of a precipitate immediately, without the action of acid, shows the presence of the latter sugars—its formation only after ebullition with acid indicating, in the absence of starch or dextrin, cane-sugar. In this reduction-process the sugar is oxidized and broken up into several substances; but the exact nature of the reaction has not been ascertained.

Dextrin also reduces the copper salt to suboxide, unless its solution is cold and very dilute. It does not, however, so act on a solution of cupric acetate acidified with acetic acid, while glucose produces with this liquid the usual red cuprous precipitate (Barfoed).

Sugar from Starch.—Boil starch with a little water and a drop of sulphuric acid as for dextrin, but continue the ebullition for several minutes; on testing a portion of the cooled liquid with iodine, and another portion with the heated alkaline solution of a copper salt, as described on page 557, it will be found that the starch has nearly all become converted into a sugar—dextrose. Maltose is also formed, at first, but by the continued action of the acid is changed to dextrose. When made on a large scale, a warm (131° F.) mixture of starch and water of the consistence of cream is slowly poured into a boiling solution of one part of sulphuric acid in one hundred of water, the whole boiled for some time, the acid neutralized by chalk, the mixture filtered, the liquid evaporated to a thick syrup and set aside; in a few days it crystallizes to a granular mass resembling honey. In this operation a small quantity of dextrin remains with the glucose; but if the process be conducted under pressure, conversion, according to Manbré, is complete. Sugar made from the starch of rice, maize, etc., is largely used for table syrups, confectionaries, bee food, and as a partial substitute for malt in brewing. It is known as *patent sugar*, *saccharine*, *maltose*, etc.

In the United States the dealers term the syrups "glucose," and the further evaporated solid product "grape-sugar." The former contain one-third or more of dextrose, about one-fifth of maltose, one-fourth or more of dextrin, and about one-sixth or one-fifth of water; the latter often contain about three-fourths of dextrose, from none up to one-third of maltose, and one-seventh or one-sixth of water.

Galactose (from milk-sugar), *Sorbinose* (from mountain-ash berries), *Inosite* (from muscles), *Mannose* (from mannite), *Gulose*, *Formose*, *β-acrose*, *Rhamnose*, *Dambose* (from a caoutchouc), and *Scyllite* (from many fish), are other glucoses.

Saccharoses, or Bioses, $C_{12}H_{22}O_{11}$.

Cane-sugar, or *Sucrose* (*Saccharum Purificatum*, B.P.), is a frequent constituent of vegetable juices. Thus it forms the chief portion of cassia-pulp (*Cassiæ-Pulpa*, B.P.), is contained in the carrot and turnip, but is most plentiful in the sugar-cane; much, however, is now obtained from the sugar-maple and beetroot. On evaporation of the juice, common *brown* or *moist sugar* crystallizes out; this by re-solution, filtration through animal charcoal, evaporation to a strong syrup, and crystallization in moulds, yields the compact crystalline conical loaves known in trade as *lump-sugar*. From a slightly less strong syrup, slowly cooled, the crystals termed *sugar-candy* are deposited, white or coloured, according to the colour of the syrup. The official syrup (*Syrupus*, B.P.) is an aqueous solution, consisting of two-thirds sugar and one-third water.

The sugar in fresh fruits is mainly cane-sugar; but by the action of the acid, or possibly of a ferment in the juice, it is gradually converted into *inverted sugar*, a variety differing from cane-sugar in being uncrystallizable, and in having an inverted or opposite influence on polarized light, twisting the ray from right to left (lævogyrate, having lævo-rotation). Ripe Hips (*Rosæ Caninæ Fructus*, B.P.) contain 30 per cent. of such sugar, besides gum and acid malates and citrates. Fruit-sugar, as gathered in the form of syrup by bees, is probably a mixture of these two varieties. It is gradually altered to a crystalline or granular mass of grape-sugar, as seen in dried fruits, such as Raisins (*Uvæ*, B.P.) and the Prune (*Prunum*, B.P.), and in solidified Honey (*Mel*, B.P.). This, the common form of grape-sugar, is dextrogyrate, and hence is sometimes termed *dextrose*, to distinguish it from lævulose. Diluted with twice its weight of water, it yields a liquid having the sp. gr. 1·101 to 1·150. Honey often contains pollen, hairs, spores, the dust and dirt from the flowers, and various flocculent matters which cause it to ferment and yield mannite, alcohol, and acetic acid; hence for use in medicine it is directed (*Mel Depuratum*, B.P.) to be clarified by melting and straining while hot through flannel previously moistened with warm water. A mixture of clarified honey 80 per cent., acetic acid 10 per cent., and water 10 per cent., is official under the name of *Oxymel* (from ὀξὺς, *oxus*, acid, and μέλι, *meli*, honey). A similar mixture of honey with acetic acid containing the soluble portions of squill-bulbs (*Scilla*, B.P.) is known as Oxymel of Squill (*Oxymel Scillæ*, B.P.). Honey or cane-sugar are the bases of the official *Confections.*

Maltose, $C_{12}H_{22}O_{11}$.—This crystallizable sugar is formed, together with dextrin, when diastase or dilute acids act upon starch. In the case of diastase it is the ultimate product, but the dilute acids may convert it into dextrose. It differs also from dextrose in its optical activity.

Both cane-sugar, maltose, and grape sugar yield alcohol and carbonic acid gas by fermentation, the cane-sugar nearly always passing into grape-sugar before the production of alcohol commences.

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Carbonic acid gas.}}{2CO_2}$$

In *bread-making*, some of the starch is converted into dextrin, and this into sugar by the ferment. The above action then goes on, the liberation of gas producing the *rising* or swelling of the mixture of flour, water, and yeast (dough)—the temperature to which the mass is subjected in the oven causing escape of most of the alcohol, and further expansion of the bubbles of carbonic acid gas in every part of the now spongy loaf. The carbonic acid gas gradually evolved when flour is worked up for bread with a mixture of dry bicarbonate of sodium and tartaric acid (best preserved by previous admixture with dried flour and a little carbonate of magnesium)—*baking-powder*—exerts similar influence. The least objectionable method of introducing carbonic acid gas, however, is that of Dauglish, whose patent aërated bread is made from flour by admixture with carbonic acid water under pressure by the aid of machinery. On removal from the cylinder, the resulting dough expands by the natural elasticity of the imprisoned carbonic acid gas, and the bake-oven completes the process. The crumb of bread is official (*Mica Panis*, P.B.). All fermented bread retains, obviously, a little alcohol, sometimes 0·25 per cent.

Action of Alkali on Sugar.—To a little solution of grape-sugar add solution of potash or soda, or solution of carbonate of potassium, and warm the mixture; the liquid is darkened in colour from amber to brown, according to the amount of sugar present. A trace of picric acid greatly intensifies the colour.

Tests.—The copper-reaction, the fermentation process, and the effect of alkalies form three good tests of the presence of grape-sugar, and, indirectly, of cane-sugar. A piece of merino or other woollen material, previously dipped in a solution of stannic chloride and dried, becomes of a brown or black colour when dipped in a solution of glucose and heated to about 300° F. by holding before a fire.

Melitose or *Melitriose* (from eucalyptus) is a triose, giving on hydrolysis galactose, dextrose, and fructose. *Meletizose* (from the larch), *Trehalose* (from Turkish manna), and *Maltose* (from starch), belong to the Saccharoses.

"*Honey-dew*" is a viscid saccharine matter occasionally met with on the leaves of the lime, maple, black alder, rose, and other trees, being a sweet principle exuded from aphides. Sometimes it is sufficiently abundant to dry and fall on the ground, forming a veritable "shower of manna." It is a mixture of cane-sugar, inverted sugar, and dextrin.

Barley-sugar is made by simply heating cane-sugar till it fuses, a change from the crystalline to the uncrystallizable condition occurring. *Treacle* (*Theriaca*, B.P.), *Molasses* or *Melasses* (from *Mel*, honey), or *Golden Syrup*, chiefly results from the application of too much heat in evaporating the syrups of the sugar-cane; it is a mixture of cane-sugar with uncrystallizable sugar and more or less colouring matter. Liquorice-root (*Glycyrrhizæ Radix*, B.P.) contains a considerable quantity of uncrystallizable sugar.

Caramel.—Heat a grain or two of sugar in a test-tube until it blackens and froths; the product is *caramel*, or *burnt sugar* (the *Saccharum Ustum* of pharmacy). It is used as a colouring agent for gravies, confectionaries, spirits, vinegar, and similar materials. It is a mixture of caramels.

Milk-sugar, or *Lactose* ($C_{12}H_{22},O_{11}H_2O$) (*Saccharum Lactis*, B.P.), the sweet principle of milk of animals, is not susceptible of alcoholic or vinous fermentation by ordinary yeast;

certain varieties of the fungus, however, convert it into alcohol. It resembles grape-sugar in reducing an alkaline solution of copper with precipitation of suboxide. It is obtained from milk by adding a few drops of acid, stirring, setting aside for the *curds* to separate, filtering, evaporating the *whey* to a small bulk, filtering again if necessary, and allowing to cool and crystallize. The deposited crude "*sugar*-sand" is afterwards refined and recrystallized. It usually occurs in trade "in cylindrical masses, two inches in diameter, with a cord or stick in the axis, or in fragments of cakes—greyish-white, crystalline on the surface and in its texture, translucent, hard, scentless, faintly sweet, gritty when chewed." Thus obtained, milk-sugar has the formula above given, but if deposited during evaporation the crystals are anhydrous, $C_{12}H_{22}O_{11}$. It is soluble in 6 parts of cold and 3 of boiling water; slightly soluble in alcohol, insoluble in ether. Powdered milk-sugar is used in pharmacy as a vehicle for potent solid medicines. Milk-sugar is convertible, by the action of dilute acids, into galactose and dextrose; these may be reunited to form milk-sugar.

Saccharic Acid, $H_2C_6H_8O_8$, or $C_4H_4(OH)_4(COOH)_2$, is the result of oxidizing sucrose, dextrose, starch, gum, and lignin by nitric acid. *Mucic acid*, isomeric with saccharic acid, may be obtained in the same way by acting on lactose, gum, and dulcite.

QUESTIONS AND EXERCISES.

Into what three classes may the carbohydrates be divided?—How is grape-sugar obtained from cane-sugar?—How are cane-sugar and grape-sugar analytically distinguished?—How is dextrose obtained from starch?—Mention the chief sources of cane-sugar.—Give chemical explanations of the processes of bread-making.—What is the difference between fruit-sugar and honey?—What is oxymel?—Describe the effect of heat on cane-sugar.—How is milk-sugar obtained? How does it differ from other sugars?—Whence are mucic and saccharic acids obtained?

Amyloses, or Amyloids, $nC_6H_{10}O_5$.

Starch ($nC_6H_{10}O_5$) is contained in large or small quantities in nearly every plant. It forms about 60–70 per cent. of wheat, and from 20 to 30 per cent. of potatoes. The starch officially recognised in the British Pharmacopœia (*Amylum*) may be that of wheat (*Triticum sativum*); maize (*Zea Mays*), and rice (*Oryza sativa*).

Processes.—Rasp or grate, or scrape with a knife, a portion of a clean raw potato, letting the pulp fall on to a piece of muslin placed over a small dish or test-glass, and then pour a slow stream of water over the pulp; minute particules or *granules* of starch pass through the muslin and sink to the bottom of the vessel, fibrous matter remaining on the sieve. This is potato-starch. Even diseased potatoes furnish good starch by this method. Wheat-starch may be obtained by tying up some flour in a piece of calico, and kneading the bag in a slow stream of water flowing from a tap, the washings running into a deep vessel, at the bottom of which the white starch collects; the sticky matter remaining in the bag is *gluten.*

The *blue starch* of the shops is artificially coloured with smalt or indigo, to neutralize the yellow tint of recently washed linen; it should not be used for medicinal purposes. Starch dried in mass splits up into curious columnar masses, resembling the basaltic pillars of Fingal's Cave in Staffa, or those of the Giant's Causeway in the North of Ireland. The cause of the phenomenon, which may also be seen in grain tin, is not conclusively known.

Gluten is the body which gives tenacity to dough and bread. It seems to be a mixture of vegetable fibrin, vegetable casein, and an albuminous matter termed glutin. These substances and gluten itself are closely allied; each contains about 16 per cent. of nitrogen. *Wheaten Flour* (*Farina Tritici*, B.P.) contains about 72 per cent. of starch and 11 of gluten, as well as sugar, gum, fine bran, water, and ash. The compactness of barley, well seen in Husked or Pearl Barley (*Hordeum Decorticatum*, B.P.), is said to be due to the large amount of vegetable fibrin present. During germination the fibrin is destroyed; hence, probably, the cretaceous character of malt. *Oatmeal*, popular as "porridge," is rich in albumenoids, or flesh-forming constituents, containing nearly 16 per cent. *Sago* is granulated starch from the Sago Palm; *tapioca* from the Bitter Cassava: each has less than 1 per cent. of albumenoids. The white translucent Rice grains are the husked seeds of *Oryza sativa.* Rice (*Oryza*) and its Flour or Ground Rice (*Oryzæ Farina*), are official in the Pharmacopœia of India. Rice is a staple article of food in tropical countries. Ground rice resembles flour of wheat in composition, but contains from 85 to 90 per cent. of starch.

Mucilage of Starch.—Mix two or three grains of starch with first a little and then more water, and heat to the boiling point; mucilage of starch (*Mucilago Amyli*, B.P.) results.

This mucilage or paste is not a true solution; by long boiling, however, a portion of the starch becomes dissolved. In the latter case the starch probably becomes somewhat altered.

Chemical Test.—To some of the mucilage add a very little free iodine; a deep-blue colour is produced.

This reaction is a very delicate test of the presence of either iodine or starch. The starch must be in the state of mucilage; hence in testing for starch the substance supposed to contain it must be first boiled with water. The solutions used in the reaction should also be cold, or nearly so, as the blue colour disappears on heating, though it is partially restored on cooling. The iodine reagent may be iodine-water or tincture of iodine. In testing for iodine, its occurrence in the free state must be ensured by the addition of a drop, or even less, of chlorine-water. Excess of chlorine must be avoided, or chloride of iodine will be formed, which does not colour starch.

The so-called *iodide of starch* scarcely merits the name of a chemical compound, the state of union of its constituents being so feeble as to be decomposed at 100° F. Substances that attack free iodine remove that element from iodide of starch. The alkalies, hydrosulphuric acid, sulphurous acid, and other reducing agents destroy the blue colour. With nitric acid starch yields an explosive compound (*Xyloïdin*) $C_{12}H_{16}(NO_2)_4O_{10}$ or $C_{12}H_{16}O_6(NO_3)_4$.

Composition of Starch Granules.—Starch granules consist mainly of *granulose*, soluble in cold water and giving an indigo colour with iodine, and *starch cellulose*, insoluble in water and giving with iodine a dirty yellow colour, with, possibly, other carbohydrates. The starch cellulose forms an external coating upon the granule, and also exists mixed with the granulose inside the granule. If this coating be broken by mechanical means, the continued application of cold water will remove all the granulose, leaving the cellulose insoluble. By the action of diastase, ptyalin, and other ferments, and by other means, the granulose may be converted into sugar and dextrin, leaving the starch cellulose unacted upon.

Microscopical Examination of Starches.

All kinds of starch afford the blue colour with iodine, showing their chemical similarity. Physically, however, the granules of different starches differ from each other; hence a careful microscopical examination of any starch, or of any powder or vegetable tissue containing starch, enables the observer to state, with a high degree of probability, the source of the starch, either at once if he has much experience, or after comparing the granules in question with authentic specimens. A glance at the accompanying eight engravings* (figs. 42 to 49) of common starches will show to what extent different starch granules naturally differ in size, shape, general appearance, distinctness and character of the rugæ, and position of the more or less central point or hilum. While from different starches individual granules may be picked out which much resemble each other, the appearance of each starch as a whole is fairly characteristic; that is to say, each *group* of granules differs in one or more characters from similar *groups* of granules of other starches.

A quarter-inch object-glass will commonly suffice for the microscopical observation of starch. A very little of the starch is mixed on a glass slide with a drop of water, a piece of thin covering-glass placed on the drop and gently pressed, so as to provide a very thin layer for observation. Instead of water, diluted spirit of wine, diluted glycerine, turpentine or other essential oil, Canada balsam, and other fluids may be used in cases where the markings or other appearances are not well defined. The illumination also of the granules may be varied, the light being reflected or transmitted, concentrated or diffused, white or coloured, polarized or plain. Polarized light is especially valuable in developing differences, and in intensifying the effects of obscure markings. By polarized light the granules of potato starch appear as if traversed by a black cross; wheat starch granules and many others also peculiarly and characteristically influence polarized light. Distinctive characters will sometimes present themselves only when the granules are made to roll over in the fluid in which they have been temporarily mounted, or when the slide is gently warmed. Starches which have already been subjected to the influence of heat, partly, as in sago or tapioca, or almost entirely, as in bread, will of course differ in appearance from granules of the same starch before being dried, cooked, or torrefied. The characters of a starch will also somewhat vary according to the age and condition of the plant yielding it.

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* By permission of Messrs. Longmans & Co., these engravings have been copied, with very few modifications, from the plates in two of the three volumes of the original edition of Pereira's "Materia Medica."

The description of the microscopical characters of the official varieties of starch is as follows:—1. Wheat starch: A mixture of large and small granules, which are lenticular in form, and marked with faint concentric striæ surrounding a nearly central hilum. 2. Maize starch: Granules more uniform in size, frequently polygonal, somewhat smaller than the large granules of wheat starch, and having a very distinct hilum but without evident concentric striæ. 3. Rice starch: Granules extremely minute, nearly uniform in size, polygonal, hilum small and without striæ.

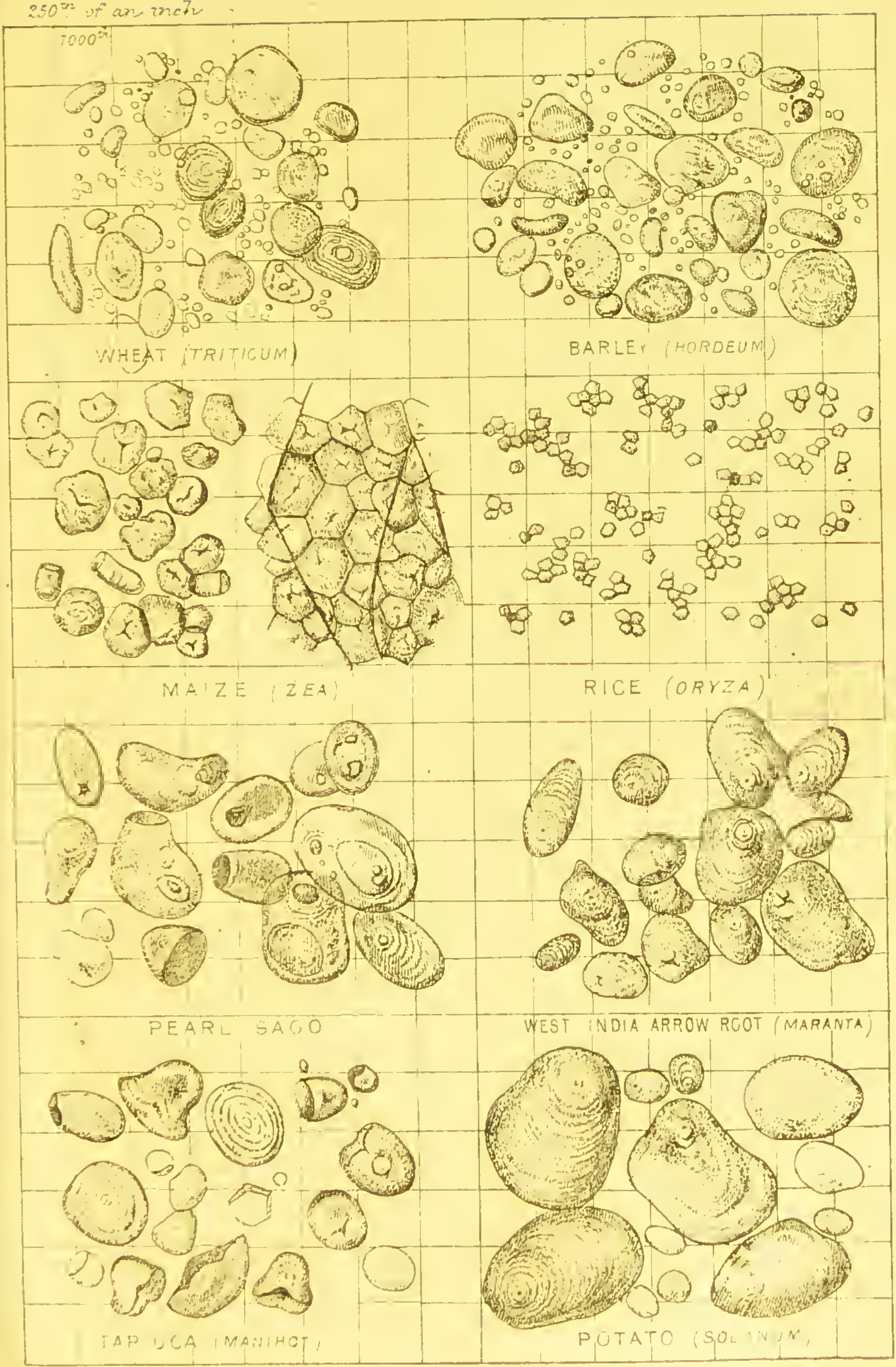
(For plates and descriptions of the characters of other starches occurring in plants used for medicinal purposes, the reader is referred to works on Materia Medica, and to the indexes of Journals of Pharmacy, as well as to general works and magazines on microscopy. For engravings of starch granules *in situ*, *vide* Berg's "Anatomischer Atlas," published by Gaertner, Berlin.)

The student may place fair confidence in the accompanying lithographs, and in most of the published engravings of starch-granules; but in microscopical analyses of importance the worker should, if possible, himself obtain actual specimens of starches for comparison from the respective seeds, fruits, and other tissues.

Inulin $(C_6H_{10}O_5)_6H_2O$ (Kiliani) is associated with simi-

STARCHES

mag^{d} 250 dia^{s}



WHEAT (TRITICUM)

BARLEY (HORDEUM)

MAIZE (ZEA)

RICE (ORYZA)

PEARL SAGO

WEST INDIA ARROW ROOT (MARANTA)

TAPIOCA (MANIHOT)

POTATO (SOLANUM)

[illegible] del.
W. West & Co. imp

lar bodies *pseudo-inulin* $(C_6H_{10}O_5)_{16}H_2O$, and *inulenin* $(C_6H_{10}O_5)_{10}2H_2O$ (Tanret). It is a white powder apparently occupying the place of starch in the roots of many plants, especially those of the natural order *Compositæ*. Twenty to forty-five per cent. has been obtained from elecampane (*Inula helenium*). It is also contained in the dahlia, colchicum, arnica, dandelion, chicory, artichoke, etc. It is soluble in boiling water, nearly all being redeposited on cooling. Iodine turns it yellow. Long ebullition converts it into a kind of gum. Like starch, inulin is convertible into sugar, but by its own special ferment, the existence of which, in the Jerusalem Artichoke, has been demonstrated by Professor J. R. Green. This ferment differs from diastase in being without the power of converting starch into sugar.

Lichenin $(nC_6H_{10}O_5)$ is a white starch-like powder largely contained in many lichens—Iceland " Moss," *Cetraria Islandica*, and many others. It is soluble in boiling water, and the fluid gelatinizes on cooling. It may be precipitated from its aqueous solution by alcohol. With iodine it gives a reddish-blue colour.

Glycogen, or *animal starch*, is the name given to the solid matter stored in the liver and resulting from the dehydration of the digested hydrated food which has been carried to the liver by the portal vein.

Dextrin, $(nC_6H_{10}O_5)$.—Mix a grain or two of starch with half a test-tubeful of cold water and a drop or two of sulphuric acid, and boil the mixture for a few minutes; no mucilage is formed, and the liquid, if sufficiently boiled, yields no blue colour with iodine; the starch has become converted into *dextrin* and some sugar. Dextrin is also produced if starch is maintained at a temperature of about 320° F. for a short time. Dextrin is now largely manufactured in the latter way, and a paste of it is used by calico printers as a vehicle for colours; it is termed *British gum*. The change may also be effected by *diastase*, a peculiar ferment existing in malt. Mix two equal quantities of starch with equal amounts of water, adding to one a little ground malt, then heat both slowly to the boiling-point: the mixture without malt thickens to a paste or pudding; that with malt remains thin, its starch having become converted into dextrin and a sugar termed maltose.

Diastase is probably a mixture, but possibly an oxidation product, of the coagulable albumenoids. It is so named from διάστασις (*diastasis*), *separation*, in allusion to the separation, or rather alteration, it effects among the constituent atoms of the molecule of starch. This function is shared by the saliva, pancreatic juice, bile, and the intestinal and other juices. The function is completely destroyed when the albumenoids are coagulated by a temperature of from 176° to 178° F.

The action of diastase upon starch.—Diastase has scarcely any action upon unbroken starch granules. The granules must be ruptured by gelatinization with heat and moisture, or in some other way. When a solution containing diastase, such as a cold water infusion of malt, is allowed to act upon gelatinous starch or starch-paste at 140° to 160° F., liquefaction occurs. It is possible to operate so that when liquefaction has taken place, the solution shall give no reaction for sugar or dextrin. If this solution be concentrated and allowed to cool, a glistening white precipitate of soluble starch falls. Soluble starch is probably the result of the partial decomposition of the more complex molecule of granulose or gelatinous starch. The next step in the action of diastase upon gelatinous starch is the breaking down of the soluble starch molecule into dextrin and a sugar called maltose. At least ten dextrins are successively produced, each simpler than the one preceding it, the proportion of maltose being correspondingly increased. The dextrins first produced give a red or brown colour with iodine, while those last produced, and having a simpler molecule, give no colour with iodine. The final reaction may be expressed thus :—

$$\underset{\text{Soluble starch.}}{10(C_{12}H_{20}O_{10})} + 8H_2O = \underset{\text{Maltose.}}{8(C_{12}H_{22}O_{11})} + \underset{\text{Dextrin.}}{4(C_6H_{10}O_5)}$$

The dextrins are distinguished by their rotatory power, their reducing action on cupric salts, and in other ways.

Starch heated with glycerine is converted into the soluble variety. The latter may be precipitated from an aqueous solution by strong alcohol. A strong solution in water gradually gelatinizes, owing to reconversion into insoluble starch. (Zulkowsky.)

The action of dilute acids upon starch.—Dilute acids act upon gelatinous starch in the same way as diastase, except that the final product is glucose.

Malt (the word malt is said to be derived from the Welsh *mall*, soft or "rotten") is simply barley which has been softened by steeping in water, allowed to germinate slightly, and further change then arrested by the application of heat in a kiln. During germination the gluten breaks up and yields a glutinous substance termed vegetable gelatine, diastase, and other matters. To the vegetable gelatine is due much of the "body" of well malted and slightly hopped beer; it is precipitated by tannic acid; hence the thinness of ale (pale or bitter) brewed with a large proportion of hop or other materials containing tannic acid. A portion of the diastase reacting on the starch of the barley converts it into dextrin, and, indeed, carries conversion to the further stage of maltose, as will be explained immediately. The temperature to which the malt is heated is made to vary, so that the sugar of the malt may or may not be partially altered to a dark-brown colouring material: if the temperature is high, the malt is said to be *high-dried*, and is used in porter-brewing; if low, the product is of lighter colour, and is used for ale. The diastase remaining in malt is still capable of converting a large quantity of starch into dextrin and sugar (maltose); hence the makers or distillers of the various spirits operate on a mixture of malted and unmalted grain in preparing liquors for fermentation.

Extract of Malt is an evaporated infusion of malt. Taken with food, its diastase aids in the conversion of starch into a variety of sugar termed maltose, and dextrin, and *pro tanto*, assists enfeebled digestive powers.

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}$$

As diastase begins to lose this power at temperatures above 150° F., that degree should not be exceeded in evaporating the infusion; indeed, if the dissolved albumenoid matters are to be retained, the evaporation should be conducted at 120° F.

The following method serves for the estimation of the diastasic power of malt extract:—1·5 gram of the extract is dissolved in 15 c.c. of water and mixed with a mucilage of ·1 gram of starch in 100 c.c. of water. The mixture is raised to 140° F. in temperature, and tested from time to time by adding two drops of iodine solution to 5 c.c. of it, and comparing with 5 c.c. of a similar mixture to which no starch has been added. No difference of tint between the two solutions indicates completion of the reaction. Good malt extract will accomplish this within half an hour, some samples will take less time, but many commercial extracts will require three hours or more.

Gum is a frequent constituent of vegetable juices, existing in large quantity in several species of Acacia. The nature of gums is very little known, though most probably they all belong to the carbohydrates. According to Fremy, gum is a calcium salt, sometimes partially a potassium salt, of the *gummic* or *arabic* radical, though consisting mostly of arabin or arabic acid alone. The formula of gummic acid is said to be $H_2C_{12}H_{18}O_{10},H_2O$, but, from the important researches of O'Sullivan, it would seem to be far more complex, a multiple of the empirical formula, $C_6H_{10}O_5$—Raoult $(C_6H_{10}O_5)_7$. Gum differs from dextrin in yielding mucic acid when oxidized by nitric acid. Good adhesive mucilages may be made from such gum-arabic substitutes as "ghatti," "amrad," etc. *Cerasin* or cherry-tree gum is a metagummate of calcium, an insoluble modification of acacia gum. *Bassorin*, *traganthin*, or *adraganthin* ($C_{12}H_{20}O_{10}$) is a form of gum which is insoluble in water, but absorbs large quantities of that liquid and forms a gelatinoid mass: it occurs largely in Tragacanth, combined, like arabin, with calcium. *Pectin*, or Vegetable Jelly ($C_{32}H_{40}O_{28}$, $4H_2O$), is the body which gives to expressed vegetable juices the property of gelatinizing: it forms the chief portion of Irish or Carrageen "Moss" (*Chondrus crispus*). *Ceylon "Moss"* (*Gracillaria lichenoides* and *G. confervoides*, P.I.) contains from one-third to three-fourths of vegetable jelly.

The mucilage of marsh-mallow root (*Althea officinalis*) and of linseed or common flax-seed (*Linum usitatissimum*) is a gum-like substance containing much mineral matter. It is the basis of the infusions formed *mallow-tea* and *linseed-tea*. Somewhat similar mucilage occurs in infusion of Bael: it is also largely yielded by the seeds of the Quince (*Pyrus Cydonia*). *Salep*, the powdered dried tubers of many species of *Orchis*, contains a large quantity of such matter. *Squill* also. The Indian *Okra* (*Hibisci Capsulæ*, P.I., from *Hibiscus esculentus*) and *Ispaghùl* or *Spogel* seeds (*Ispaghulæ semina*, P.I., from *Plantago ispaghula*) also appear to contain a considerable quantity.

Cellulin, or *cellulose*, $C_6H_{10}O_5$, the woody fibre of plants, familiar, in the nearly pure state, under the forms of "cotton-wool" (*Gossypium*, B.P., hairs of the seed of various species of Gossypium), paper, linen, and pith, is another substance isomeric, probably polymeric, with starch. Lignin is a closely allied body, lining the interior of woody cells and vessels. By the action of nitric acid of various strengths on cellulin, mono-, di-, or tri-nitrocellulins are readily formed :— $C_6H_9O_4NO_3$, $C_6H_8O_3(NO_3)_2$, $C_6H_7O_2$, $(NO_3)_3$. Trinitrocellulin is highly-explosive gun-cotton ; dinitrocellulin is not sufficiently explosive for use instead of gunpowder; mononitrocellulin is scarcely at all explosive. The heat of a waterbath may explode trinitrocellulin, but not dinitrocellulin if pure. The three displaceable atoms of hydroxyl in cellulin may be displaced by bodies other than the nitric radical.

Dinitrocellulin (*Pyroxylin*, B.P.) may be prepared by the following official process :—Mix five fluid ounces of sulphuric acid and five of nitric in an earthenware mortar, immerse 1 ounce of cotton-wool in the mixture, and stir it for three minutes with a glass rod, so that it is thoroughly and uniformly wetted by the acids. Transfer the cotton to a vessel containing a considerable volume of water, stir it rapidly and well with a glass rod, decant the liquid, pour more water upon the mass, agitate again, and repeat the affusion, agitation, and decantation until the washings cease to give a precipitate with chloride of barium. Drain the product on filtering paper, and dry on a water-bath.

Pyroxylin may also be made by soaking 7 parts of white filtering-paper, which has been washed in hydrochloric acid and dried, in a mixture of 140 parts of sulphuric acid (sp. gr. 1·82) and 70 of nitric acid (1·37) for three hours, and well washing the product (Guichard).

Mononitrocellulin and *trinitrocellulin* are insoluble in a mixture of alcohol and ether ; *dinitrocellulin* or *pyroxylin* is soluble, the solution forming ordinary collodion (*Collodium*, B.P.). The official proportions are 1 oz. of pyroxylin dissolved in a mixture of 36 fl. oz. of ether and 12 of rectified spirit. After digesting for a few days, decant the liquid from any sediment and preserve it in a well-corked bottle. It dries rapidly upon exposure to the air, and leaves a thin, transparent film, insoluble in water or spirit. Flexible collodion (*Collodium Flexile*, B.P.) is a mixture of collodion (48 fluid parts), Canada balsam (2 parts), and castor oil (1 part). *Blistering Collodion* (*Collodium Vesicans*, B.P.) is a solution of pyroxylin in acetic ether containing the active blistering principle of cantharides. Many articles of utility and beauty are now made of pyroxylin variously coloured and sold under the name of *xylonite* (ξύλον, *xulon*, wood) or *celluloid* (cellulin-like).

Tunicin, or animal cellulose, exists.

Isomerism. Allotropy. Polymorphism.

The composition of dextrin is represented by the same formula as that of starch, namely $C_6H_{10}O_5$; for it has the same percentage composition as starch. Inulin (p. 566) and cellulose (p. 571) have also a similar formula. There are many other bodies similar in centesimal composition, but dissimilar in properties; such substances are termed *isomeric* (from ἴσος, *isos*, equal, and μέρος, *meros*, part; and their condition is spoken of as one of *isomerism*. There is sometimes good reason for doubling or otherwise multiplying the formula of one of two *isomers*, *isomerides*, or isomeric bodies. Thus a molecule of ethylene (olefiant gas), the chief illuminating constituent of coal-gas, is represented by the formula C_2H_4, while a molecule of amylene, an anæsthetic liquid hydrocarbon, obtained from amylic alcohol, though having the same percentage composition as olefiant gas, is represented by the formula C_5H_{10}; for amylene, when gaseous, is about twice and a half as heavy as ethylene, and must contain, therefore, in each molecule, twice and a half as many atoms, for (Avogadro) these equal volumes must contain equal numbers of molecules; its formula is, consequently, constructed to represent those proportions. (Read again pages 29 to 60.) This variety of isomerism is termed *polymerism* (from πολὺς, *polūs*, many or much, and μέρος, part). Formic aldehyde, CH_2O; acetic acid, $C_2H_4O_2$, and lactic acid, $C_3H_6O_3$, are, obviously, *polymers*. Metastannic acid (*vide* p. 275) is a polymeric variety, or *polymeride*, of stannic acid.

An illustration of a second variety of isomerism is seen in the case of cyanate of ammonium and urea, bodies already alluded to in connection with cyanic acid. These and several other pairs of chemical substances have dissimilar properties, yet are similar, in elementary composition and in the centesimal proportion of the elements, and we cannot escape the conclusion that each molecule possesses the same number of atoms. But the reactions of these bodies indicate the probable nature of their construction; and this is shown in their formulæ by the disposition of the symbols. Thus cyanate of ammonium is represented by the formula NH_4CNO, urea by $CO(NH_2)_2$. Such bodies are termed *metameric* (from μετά, *meta*, a preposition denoting change, and μέρος), and their condition spoken of as one of *metamerism*. For two metameric nitro-methylic and also two nitro-ethylic bodies see p. 483. Acetate of ethyl (p. 484) is metameric with butyric acid (p. 582), for they have the same percentage composition and their vapours have the same specific gravity, and each therefore might be represented by the formula $C_4H_8O_2$; but their properties warrant us in assuming that their atoms occupy different positions in the two molecules—justify us in giving $CH_3CO{\cdot}OC_2H_5$ as a picture of a molecule of acetate of ethyl, and C_3H_7COOH as a picture of a molecule of butyric acid. Acetate of methyl ($CH_3COO{\cdot}CH_3$), propionic acid (C_2H_5COOH),* and formate of ethyl ($H{\cdot}CO{\cdot}OC_2H_5$) are isomers of the metameric variety, or *metamers*, or *metamerides*; also quinine and quinidine, cinchonine and cinchonidine, and many of the volatile oils, etc. The isomerism of starch and dextrin may be of a polymeric or of a metameric character; but we do not yet know which, and must therefore at present give them identical formulæ, though it is most probable that many of the carbohydrates are multiples of the mere empirical formulæ, since dextrin ($xC_6H_{10}O_5$) by hydration, produces maltose, $C_{12}H_{22}O_{11}$, which would point to the formula of dextrin as being at least $(C_6H_{10}O_5)_2$, while the extent to which it lowers the freezing point of a solvent points to $(C_6H_{10}O_5)_7$. Patient accumulation of facts and the aid of the theory of valency will, doubtless, sooner or later, fully explain all cases of isomerism.

Substances similar in composition and constitution, yet differing in properties, are termed *allotropic* (ἄλλος, *allos*, another, τρόπος, *tropos*, condition). Thus ordinary phosphorus, kept at a temperature of about 450° F., in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. (red, or amorphous phosphorous). A black allotropic variety of phosphorus is known. There are also three *allotropes* of carbon which are respectively crystalline, graphitic, and amorphous. Sulphur may be obtained in the viscous as well as in the hard, brittle condition. Another illustration of *allotropy* is seen in the varieties of tartaric acid which have different optical properties, but otherwise are identical; they are in neither of the above-mentioned states of isomerism, but are allotropic modifications of the same substance. The constitution of such bodies is perhaps best conceived by the aid of stereochemical hypotheses. Occasionally one and the same substance crystallizes in two distinct forms; its state is then described as one of *polymorphism* (πολυς, *polus*, many; μορφὴ, *morphe*, form). Sulphur is polymorphous. It crystallizes by slow cooling in (1) prismatic crystals of sp. gr. 1·98, while in Nature it occurs in (2) octahedra of sp. gr. 2·07. Melted and poured into water, sulphur takes up (3) the form of caoutchouc of sp. gr. 1·96. These differences warrant the statement that sulphur occurs in three distinct allotropic conditions. Possibly such conditions result from the association of different numbers of atoms in the molecule of the element; that is, allotropic bodies may simply be *physically polymeric*, or in some other way be mere *physical isomerides.*

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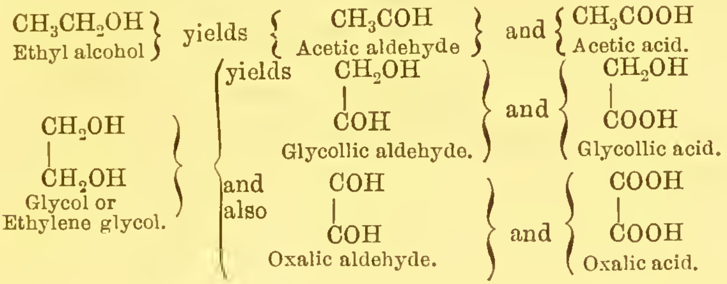
* For explanation of formulæ, see section on Aldehydes and Acids, p. 475.

QUESTIONS AND EXERCISES.

How is wheat-starch or potato-starch isolated?—Define gluten and glutin.—Enumerate the proximate principles of wheaten flour.—Is starch soluble in water?—Which is the best chemical test for starch?—Distinguish physically between the varieties of starch.—Into what compound is starch converted by heat?—What occurs when a mixture of starch and water is allowed to flow into hot diluted sulphuric acid?—If two equal amounts of starch with water be heated, one containing a small quantity of ground malt, what effects ensue?—Write a short article on the chemistry of malting.—What is the nature of gum arabic? and how is it distinguished from "British gum"?—Mention the properties of the products of the action of nitric acid of various strengths on cellulin.—How is pyroxylin prepared?—Explain *isomerism*, giving several illustrations.—Give examples of polymeric bodies.—State the formula of a body metameric with urea.—Define allotropy and polymorphism, giving illustrations.

ALDEHYDES AND ACIDS.

General Formation.—The aldehydes and acids may be artificially formed by oxidation of the primary alcohols, glycols, etc. Monhydric alcohols, having only one hydroxyl (OH) group, form monobasic acids, dihydric alcohols (glycols) having two hydroxyl groups, yield monobasic and dibasic acids; and so on. Thus:—



$$\left.\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}\right\} \text{ yields } \left\{\underset{\text{Acetic aldehyde}}{CH_3COH}\right\} \text{ and } \left\{\underset{\text{Acetic acid.}}{CH_3COOH}\right.$$

$$\left.\underset{\text{Glycol or Ethylene glycol.}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}}\right\} \left\{\begin{array}{l} \text{yields } \left\{\underset{\text{Glycollic aldehyde.}}{\begin{matrix}CH_2OH\\|\\COH\end{matrix}}\right\} \text{ and } \left\{\underset{\text{Glycollic acid.}}{\begin{matrix}CH_2OH\\|\\COOH\end{matrix}}\right. \\ \text{and also } \left\{\underset{\text{Oxalic aldehyde.}}{\begin{matrix}COH\\|\\COH\end{matrix}}\right\} \text{ and } \left\{\underset{\text{Oxalic acid.}}{\begin{matrix}COOH\\|\\COOH\end{matrix}}\right. \end{array}\right.$$

It will be seen that the groups COH and COOH denote respectively an aldehyde and an acid, the H in the COOH group being replaceable by a metal, such as $CH_3{\cdot}CO{\cdot}ONa$ (acetate of sodium). *See* also pages 488 and 543.

Acids may also be obtained by acting on the *nitriles* or cyanides of the hydrocarbon radicals with hydrochloric acid and water. Thus:—

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Monochloro-methane.}}{CH_3Cl} + \underset{\text{Hydrochloric acid.}}{HCl}$$

$$\underset{\text{Monochloro-methane.}}{CH_3Cl} + \underset{\text{Cyanide of potassium.}}{KCN} = \underset{\text{Cyanide of methyl or acetonitrile.}}{CH_3CN} + \underset{\text{Chloride of potassium.}}{KCl}$$

$$\underset{\text{Acetonitrile.[*]}}{CH_3CN} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Acetic acid.}}{CH_3COOH} + \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

Many aldehydes and acids occur in Nature; for example, oil of meadow-sweet (salicylic aldehyde), oil of bitter almonds (benzoic aldehyde), citric acid in lemons.

General Reactions.—Aldehydes all form crystalline compounds with acid sulphite of potassium, by oxidation they yield an acid, and by the action of nascent hydrogen they yield an alcohol, while acids, by nascent hydrogen, yield an aldehyde and then an alcohol. With oxides, hydrates, carbonates, and sometimes with metals, acids form metallic derivatives. With the alcohols, acids yield alkyl* or ethereal salts, as, for instance, acetic ether. By the action of the chloride, iodide, or bromide of phosphorus their hydroxyl group is replaced by chlorine, iodine, or bromine:—

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[*] The reactions of *nitriles* indicate that the radical present is united to the carbon of the cyanogen, while the reactions of *isonitriles* (or *carbamines*) indicate that the radical is united to the nitrogen. Hence such formulæ as CH_3CN and CH_3NC.

$$\underset{\text{Acetic acid.}}{3CH_2COOH} + \underset{\text{Phosphorus trichloride.}}{PCl_3} = \underset{\text{Chloride of acetyl.}}{3CH_3CO{\cdot}Cl} + \underset{\text{Phosphorous acid.}}{PO_3H_3}$$

Like inorganic acids, they form anhydrides by the elimination of water:—

$$\underset{\text{Acetic acid.}}{2CH_3COOH} - \underset{\text{Water.}}{H_2O} = \underset{\text{Acetic anhydride.}}{\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right\}O}$$

The important aldehydes and acids will now be mentioned.

The Acetic Series.

Acids of the Acetic Series, $C_nH_{2n+1}CO{\cdot}OH$ (Monobasic).—Formed by the two general methods given, namely, from primary alcohols of the ethylic series and from cyanides of the paraffin hydrocarbon radicals.

Formic Acid, $H{\cdot}COOH$. Formic aldehyde, $H{\cdot}COH$. *See* p. 394.

Acetic Acid, CH_3COOH (Methylformic acid). Obtained by the oxidation of alcohol and in other ways. *See* p. 347.

Aldehyde, or Acetic Aldehyde, C_2H_4O, or CH_3COH.

Preparation.—Place together, in a capacious test-tube or flask, about four parts of spirit of wine, six of black oxide of manganese, six of sulphuric acid, and four of water, and gently warm the mixture; aldehyde (*al*cohol *dehyd*rogenatum), a highly volatile liquid, is immediately formed, and its vapour evolved, recognised by its peculiar, somewhat fragrant odour. Adapt a cork and rather long bent tube to the test-tube, and let some of the aldehyde slowly distil over into another test-tube, the condensing-tube being kept as cool as possible. Set the distillate aside for a day or two; the aldehyde will have nearly all disappeared, and acetic acid be found in the tube. Test the exposed liquid by litmus-paper; it will be found to have an acid reaction: make it slightly alkaline by a drop or two of solution of carbonate of sodium, then boil to remove any alcohol and aldehyde present, add sulphuric acid, and notice the characteristic odour of the acetic acid evolved.

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* *Alkyl Salts. Alkyl*, from the Arabic article *al*, the, as in alkali, alcohol, etc., and the termination common to the names of such radicals as ethyl, amyl, and phenyl, and as seen in methyl, the prototype of such names. (See p. 521.) In Germany the word *ester*, a mere variation of the word *ether*, is similarly employed. In the scientific chemistry of both countries it is thus sought to restrict the name *ethers* to the oxides of radicals, as common ether $(C_2H_5)_2O$ (*Æther*, B.P.).

These experiments will enable the process of acetification described in connection with acetic acid to be more fully understood. Pure diluted alcohol is not oxidized by exposure to air alone; but in presence of a ferment, *bacterium aceti*, it is oxidized first to aldehyde and then to acetic acid.

In the above process the black oxide of manganese and sulphuric acid furnish nascent oxygen:—

$$\underset{\substack{\text{Black oxide}\\\text{of manganese.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphate of}\\\text{manganese.}}}{MnSO_4} + \underset{\substack{\text{Oxygen}\\\text{(atom).}}}{O} + \underset{\text{Water.}}{H_2O}$$

The nascent oxygen then acts on the alcohol, just as the oxygen of the air acts on the alcohol in fermented infusion of malt, beer, or wine, giving aldehyde:—

$$\underset{\text{Alcohol.}}{CH_3CH_2OH} + \underset{\substack{\text{Oxygen}\\\text{(atom).}}}{O} = \underset{\text{Aldehyde.}}{CH_3COH} + \underset{\text{Water.}}{H_2O}$$

The aldehyde rapidly, even when pure (more rapidly when impure), absorbs oxygen and yields acetic acid:—

$$\underset{\text{Aldehyde.}}{2CH_3COH} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{2CH_3COOH}$$

Tests.—Aldehyde heated with solution of potash gives a brownish-yellow resinous mass of peculiar odour. Its aqueous solution reduces salts of silver, giving a mirror-like coating to the cleaned sides of a test-tube. When acted on by phenol dissolved in sulphuric acid, it gives a red colour. Aldehyde on keeping, or in contact with sulphuric acid, chloride of zinc, etc., yields two polymerides—metaldehyde, (xC_2H_4O), and paraldehyde, $C_6H_{12}O_3$, the latter having a characteristic odour. The official paraldehyde (*Paraldehydum*, B.P.) boils at 124° C., should not melt under 10° C., dissolves in water, spirit or ether, is neutral, and if it contains no ordinary aldehyde, will not be coloured on standing for two hours with solution of potash or soda.

CHLORAL.

Chloral, or *trichloraldehyde*, CCl_3COH, is a chlorine substitution derivative of aldehyde, though it cannot directly be obtained by acting on aldehyde by chlorine, because condensation products are formed.

Process.—Pass a rapid stream of dry chlorine into pure absolute alcohol so long as absorption occurs. During the first hour or two the alcohol must be kept cool, afterwards gradually warmed till ultimately the boiling-point is reached. The preparation of a considerable quantity occupies several days. The crude product is mixed with three times its volume of sulphuric acid and distilled, again mixed with a similar quantity of sulphuric acid and again distilled, and finally rectified from quicklime.

The formation of chloral would at first sight seem to be due to the production from the alcohol (CH_3CH_2OH) of aldehyde (CH_3COH), through the removal of hydrogen by the chlorine, and the substitution of chlorine for hydrogen in the aldehyde (CH_3COH) with formation of *chlor-aldehyde* or *chloral* (CCl_3COH). But the reactions are far more complicated, being as follows:—

Aldehyde and hydrochloric acid are first formed:—

$$\underset{\text{Alcohol.}}{CH_3CH_2OH} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Aldehyde.}}{CH_3COH} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

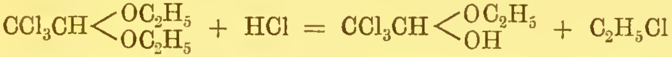
The nascent aldehyde unites with alcohol, forming acetal:—

$$\underset{\text{Aldehyde.}}{CH_3COH} + \underset{\text{Alcohol.}}{2C_2H_5OH} = \underset{\text{Acetal.}}{CH_3{\cdot}CH{\cdot}(OC_2H_5)_2} + \underset{\text{Water.}}{OH_2}$$

Acetal* by further chlorination yields trichloracetal:—

$$\underset{\text{Acetal.}}{CH_3{\cdot}CH(OC_2H_5)_2} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Trichloracetal.}}{CCl_3CH{\cdot}(OC_2H_5)_2} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

Trichloracetal when acted on by hydrochloric acid yields ethyl chloride and chloral alcoholate:—



$$\underset{\text{Trichloracetal.}}{CCl_3CH{<}{\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}}} + HCl = \underset{\text{Chloral alcoholate.}}{CCl_3CH{<}{\begin{smallmatrix}OC_2H_5\\OH\end{smallmatrix}}} + \underset{\text{Ethyl chloride.}}{C_2H_5Cl}$$

From the alcoholate, chloral is liberated by treatment with sulphuric acid:—

$$\underset{\text{Chloral alcoholate.}}{CCl_3{\cdot}CH{\cdot}(OC_2H_5)OH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Chloral.}}{CCl_3COH} + \underset{\text{Ethyl-hydrogen sulphate.}}{C_2H_5HSO_4} + \underset{\text{Water.}}{OH_2}$$

Properties.—It is a colourless liquid, of oily consistence. Sp. gr. 1·502. Boiling-point 201·2° F. Its vapour has a penetrating smell, and is somewhat irritating to the eyes. Mixed with water, heat is disengaged, and solid white, crystallizable, *chloral hydrate*, $CCl_3CH(OH)_2$, or *Hydrate of Chloral* (*Chloral Hydras*, B.P.), results. "Chloral hydrate" is a true glycol, the water not being simply water of crystallization but of combination, the systematic name being trichlorethylidene glycol:—

$$\underset{\text{Ethylene glycol.}}{C_2H_4(OH)_2} \qquad \underset{\text{Trichlorethylidene glycol.}}{CCl_3CH(OH)_2}$$

Chloral hydrate fuses when heated, solidifies at about 120° F., boils at from 202° to 206° F. It sublimes as a white crystalline powder. Both chloral and chloral hydrate are soluble in water, alcohol, ether, and oils. Oils and fats are also soluble in chloral hydrate. The aqueous solution should be neutral, and give no reaction with nitrate of silver. Chloral, especially if it contains a trace of acid, may undergo a spontaneous change into an opaque white isomeric modification, *metachloral*, insoluble in water, alcohol, or ether, but convertible by prolonged contact with water or by distillation into the ordinary condition. By action of weak alkalies chloral yields formate of the alkali-metal and chloroform:—

---

* *Methylal*, $CH_2(OCH_3)_2$, the lowest term of the series, is occasionally used as a soporific.

$$CCl_3COH + KOH = H{\cdot}CO{\cdot}OK + CHCl_3.$$

Chloral, or rather strong aqueous solution of chloral hydrate (3 in 4), injected beneath the skin yields chloroform, and produces narcotic effects (Liebreich, Personne). Chloroform itself admits of similar hypodermic use (Richardson). If administered by the stomach, thirty to eighty grains of solid hydrate are required. The final products of the reaction of the chloroform and blood are formate and chloride of sodium. A strong spirituous solution of potash effects the same transformation:—$CHCl_3 + 4KOH = H{\cdot}COOK + 3KCl + 2H_2O$.

Solution of ammonia and moist hydrate of calcium, as well as weak solutions of fixed alkalies, convert hydrate of chloral into formate of the metal and chloroform. The reaction with the slaked lime being especially definite and complete (Wood), it may be employed in ascertaining the richness of a sample of commercial chloral hydrate in chemically pure chloral hydrate.

$$\underbrace{2(CCl_3CH(CH)_2)}_{331} + Ca2OH = \underbrace{2CHCl_3}_{239} + (HCOO)_2Ca + 2H_2O.$$

From the foregoing equation and molecular weights, it is obvious that 100 grains of hydrate of chloral, if quite dry, will yield by distillation with 30 grains of slaked lime and an ounce of distilled water (in a small flask and long bent tube kept cool by moistened paper) 72·2 grains of chloroform by weight, or (the sp. gr. of chloroform being taken at 1·497) 47·56 grains by measure, or about 52 minims. 100 grains of the official hydrate of chloral "should yield not less than 70 grains of chloroform." (Any such definite quantity of chloroform, on account of its volatile nature, is perhaps best measured, the weight being obtained by multiplying the volume by 1·5.)

Small quantities of chloral hydrate in dilute solutions may be estimated by converting its chlorine into hydrochloric acid by nascent hydrogen, and titrating with volumetric solution of nitrate of silver (Short). A quantity of solution containing not more than ·05 of a gram is placed in a small flask with granulated zinc and acetic acid, and allowed to stand twenty-four hours; the solution is then poured off and the zinc washed two or three times with distilled water, a little yellow chromate of potassium is added, and it is then titrated with decinormal nitrate of silver solution in the usual way, the acetic acid and acetate of zinc not interfering with the indications. 1,000 c.c. of the silver solution indicate 5·52, nearly, of chloral hydrate.

Pure Chloral Hydrate.—Liebreich, who first proposed the use of chloral hydrate, gives the following as the characteristics of a pure article:—Colourless, transparent crystals. Does not decompose by the action of the atmosphere, does not leave oily spots when pressed between blotting-paper, affects neither cork nor paper. Smells agreeably aromatic, but a little pungent when heated. Tastes bitter, astringent, slightly caustic. Seems to melt on rubbing between the fingers. Dissolves in water like candy without first forming oily drops; and the solution is neutral or faintly acid to test-paper. Dissolves in bisulphide of carbon, petroleum, ether, water, alcohol, oil of turpentine, etc. Its solution in chloroform gives no colour when shaken with sulphuric acid. Boiling-point 203° to 205° F. It volatilizes without residue. Distilled with sulphuric acid, the chloral should pass over at 205° to 207° F. Melting-point 133° to 136° F., again solidifying at about 120°. Gives no chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Impure Chloral Hydrate.—Yellowish, cloudy. Decomposes; leaves spots by pressing between blotting-paper; decomposes corks and paper of the packing. Smells pungent and irritating; on opening the bottle is sticky and often emits fumes. Taste strongly caustic. With water forms oily drops or is partially insoluble. Boils at a higher temperature. On treating it with sulphuric acid turns brown, with formation of hydrochloric acid. Gives chlorine reaction on treating the solution in water (acidulated by nitric acid) with nitrate of silver.

Alcoholates of chloral are obtained on combining alcohols with chloral. Chloral alcoholate or trichlorethylidene ethyl ether, $CCl_3CH{<}\begin{smallmatrix}OH\\OC_2H_5\end{smallmatrix}$, is obtained by mixing alcohol with chloral, it is in fact "chloral hydrate" with one hydroxyl group replaced by (OC_2H_5).

Bromal, CBr_3COH, *hydrate of bromal*, $CBr_3CH(OH)_2$, and *alcoholates of bromal*, are produced when bromine instead of chlorine attacks alcohol. *Iodal*, CI_3COH, also exists.

Butyl Chloral, $C_3H_4Cl_3COH$, originally, but erroneously, termed *croton chloral*, is a product of the action of dry chlorine on cold aldehyde. Its name expresses its constitution; it is *chlorinated butyric aldehyde*—ordinary chloral being chlorinated acet-aldehyde. *Butyl-chloral hydrate*, *croton-chloral hydrate* wrongly so called, *hydrate of butyl-chloral* (*Butyl-chloral Hydras*, B.P.), *hydrous butyl chloral*, $C_3H_4Cl_3CH(OH)_2$ (*trichlorbutylidene glycol*), occurs "in pearly white crystalline scales, having a pungent but not acid odour, resembling that of hydrous chloral, and an acrid nauseous taste. It fuses at about 172° F. (77·8° C.) to a transparent liquid, which in cooling commences to solidify at about 160° F. (71·1° C.). Soluble in about fifty parts of water, in its own weight of glycerine and of rectified spirit, and nearly insoluble in chloroform. The aqueous solution is neutral or but slightly acid to litmus-paper. It does not yield chloroform when heated with solutions of potash or soda or with milk of lime."

The Acetic Series of Acids,—continued.

Propylic or *Propionic Acid* (ethyl-formic acid), C_2H_5COOH, is produced by oxidation of propylic alcohol.

Butyric or *Tetrylic Acid* (propyl-formic acid), C_3H_7COOH, is formed by general methods; also during the fermentation of cheese. It is found as a glyceric salt in butter (whence its name).

Pentylic, *Valerianic* or *Valeric Acid*, C_4H_9COOH.—There are several varieties of this acid, the valerianic acid from valerian and angelica root, and that artificially formed from amylic alcohol (*vide* p. 429), being the iso-primary valerianic acid, or iso-propylacetic acid, $CH(CH_3)_2CH_2{\cdot}COOH$, the normal having the constitution of $CH_3CH_2CH_2CH_2{\cdot}COOH$.

Palmitic Acid, $C_{15}H_{31}COOH$, from fats; *stearic acid*, from suet, $C_{17}H_{35}COOH$; *cerotic acid*, $C_{26}H_{53}COOH$, from beeswax; and *melissic acid*, $C_{29}H_{59}COOH$, from beeswax and from canauba wax (from the leaves of *Copernicia cerifera*, a Brazilian palm), belong to the acetic series.

The Lactic Series.

Acids of the Lactic Series, $C_nH_{2n}(OH)COOH$.—This series is formed of hydroxy-derivatives of the acetic series, one atom of hydrogen being replaced by the hydroxyl group.

CH_3COOH	$CH_2(OH)COOH$
Acetic acid.	Hydroxyacetic or glycollic acid.

Though they possess only one carboxyl (COOH) group, yet, having an alcoholic hydroxyl group, they may sometimes form di-substitution derivatives with the metals.

They are best formed by hydrolysis of the nitriles produced on combining hydrocyanic acid with aldehydes or ketones; also by partial oxidation of glycols by diluted nitric acid; and by acting on monochloro-derivatives of the acids of the acetic series by moist silver oxide:—

$$\underset{\text{Monochloracetic acid.}}{2CH_2Cl{\cdot}COOH} + Ag_2O + H_2O = \underset{\text{Glycollic acid.}}{2CH_2OH{\cdot}COOH} + 2AgCl$$

Carbonic Acid or *Hydroxyformic Acid*, $OH{\cdot}CO{\cdot}OH$, the first of this series, has been studied already. *Carbamide* or *Urea*, $NH_2{\cdot}CO{\cdot}NH_2$, the normal amide of carbonic acid, is interesting historically as being the first organic body synthetically produced from inorganic sources. (*See* Index, "Urea, Artificial production of.") The acid amide of carbonic acid, *carbamic acid*, $NH_2{\cdot}CO{\cdot}OH$, occurs as an ammonium salt, $NH_2{\cdot}CO{\cdot}ONH_4$, in the carbonate of ammonium of pharmacy. The carbamate of ethyl, or *Urethane*, $NH_2{\cdot}CO{\cdot}OC_2H_5$, is a mild hypnotic.

Glycollic Acid (Hydroxyacetic acid), $CH_2OH{\cdot}COOH$, is found in the leaves of the Virginia Creeper; artificially it may be obtained by carefully oxidizing glycol, and by the action of silver oxide on dextrose and lævulose.

Lactic Acid (Hydroxypropionic acid), $C_2H_4(OH)COOH$. At least three isomeric lactic acids are known; the fermentative lactic acid (ethylidene* lactic acid) $CH_3CH{\cdot}(OH)COOH$ (*see* p. 410), and sarcolactic acid, from flesh, being those of importance.

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* Bodies having the CH_3CH group are called ethylidene compounds. Compare chloral hydrate, trichlor*ethylidene* glycol, $CCl_3CH{\cdot}(OH)_2$.

TABLE SHOWING THE RELATIONS OF THE CHIEF ACIDS OF THE ACETIC, LACTIC, AND GLYOXYLIC SERIES.

Acids of the Acetic Series, $C_nH_{2n+1}CO{\cdot}OH$.		Acids of the Hydroxyacetic or Lactic Series, $C_nH_{2n}(OH)CO{\cdot}OH$.		Acids of the Dihydroxyacetic or Glyoxylic Series, $C_nH_{2n-1}(OH)_2COOH$.	
Methylic or Formic	$H{\cdot}CO{\cdot}OH$	Hydroxyformic or Carbonic	$OH{\cdot}CO{\cdot}OH$		
Ethylic or Acetic	$CH_3{\cdot}CO{\cdot}OH$	Hydroxyacetic or Glycollic	$CH_2OH{\cdot}CO{\cdot}OH$	Dihydroxyacetic or Glyoxylic	$CH(OH)_2COOH$
Propylic or Propionic	$C_2H_5{\cdot}CO{\cdot}OH$	Hydroxypropionic or Lactic	$C_2H_4OH{\cdot}CO{\cdot}OH$	Dihydroxypropionic or Glyceric	$C_2H_3(OH)_2COOH$
Tetrylic or Butyric	$C_3H_7{\cdot}CO{\cdot}OH$	Hydroxybutyric	$C_3H_6OH{\cdot}CO{\cdot}OH$	Dihydroxybutyric	$C_3H_5(OH)_2COOH$
Pentylic or Valeric	$C_4H_9{\cdot}CO{\cdot}OH$	Hydroxypentylic	$C_4H_8OH{\cdot}CO{\cdot}OH$		
Hexylic or Caproic	$C_5H_{11}{\cdot}CO{\cdot}OH$	Hydroxycaproic or Leucic	$C_5H_{10}OH{\cdot}CO{\cdot}OH$		
Heptylic or Œnanthylic	$C_6H_{13}{\cdot}CO{\cdot}OH$	Hydroxyheptylic	$C_6H_{12}OHC{\cdot}O{\cdot}OH$		
Octylic or Caprilic	$C_7H_{15}{\cdot}CO{\cdot}OH$	Hydroxyoctylic	$C_7H_{14}OH{\cdot}CO{\cdot}OH$		
Nonylic or Pelargonic	$C_8H_{17}{\cdot}CO{\cdot}OH$				
Capric . . .	$C_9H_{19}{\cdot}CO{\cdot}OH$				
Lauric . . .	$C_{11}H_{23}{\cdot}CO{\cdot}OH$	Hydroxydodecylic	$C_{11}H_{22}OH{\cdot}CO{\cdot}OH$		
Myristic . .	$C_{13}H_{27}{\cdot}CO{\cdot}OH$				
Palmitic . .	$C_{15}H_{31}{\cdot}CO{\cdot}OH$				
Stearic . .	$C_{17}H_{35}{\cdot}CO{\cdot}OH$				
Arachidic . .	$C_{19}H_{39}{\cdot}CO{\cdot}OH$				
Behenic . .	$C_{21}H_{43}{\cdot}CO{\cdot}OH$				
Cerotic . .	$C_{26}H_{53}{\cdot}CO{\cdot}OH$				
Melissic . .	$C_{29}H_{59}{\cdot}CO\ OH$				

The Acrylic Series.

Acids of the Acrylic Series, $C_nH_{2n-1}COOH$.

Acrylic Acid, C_2H_3COOH, or $CH(CH_2)COOH$, is formed by oxidizing acrolein (acrylic aldehyde, *see* Glycerine) by oxide of silver.

Crotonic Acid, or methacrylic acid, C_3H_5COOH, or $CH(CHCH_3)COOH$, formerly supposed to be a constituent of croton oil, may be formed by oxidizing crotonic aldehyde, and by acting on allyl cyanide, C_3H_5CN, by water and hydrochloric acid:—$C_3H_5CN + 2H_2O + HCl = C_3H_5CO{\cdot}OH + NH_4Cl$.

Oleic Acid $C_{18}H_{34}O_2$, or $CH(C_{16}H_{32})COOH$, is found as a glyceric salt in many fats and oils.

Preparation.—Olive oil is saponified with caustic potash and the resulting soap decomposed by tartaric acid, which liberates oleic and stearic acids. The oleic and stearic acids are heated with lead oxide, forming lead oleate and stearate, the former being dissolved out from the latter by ether. The ether is evaporated and the lead oleate treated with hydrochloric acid, which liberates the oleic acid.

Elaidic Acid (isomeric with oleic acid) is formed by passing nitrogen peroxide into oleic acid; it is more stable than oleic acid, distilling unchanged.

The Benzoic or Aromatic Series.

Acids of the Benzoic or Aromatic Series, $C_nH_{2n-7}COOH$.—The acids of this series are formed by oxidizing hydrocarbons, by oxidation of alcohols of the benzylic series, and by acting on the cyanides of the members of the benzene series. All the acids of this series, with the exception of benzoic acid, possess many isomers.

Benzoic Acid, C_6H_5COOH, occurs naturally in gum benzoin (Gum Benjamin), which contains from 12 to 15 per cent., the rest being mainly composed of two resins having the formulæ $C_{40}H_{46}O_9$ and $C_{30}H_{40}O_5$. Benzoic acid may be obtained by oxidizing benzoic aldehyde, C_6H_5COH, which may be prepared from trichloromethylbenzene (*see* Toluene, p. 515). Benzöene (toluene) $C_6H_5CH_3$, may be directly oxidized into benzoic aldehyde, the methyl group (CH_3) being resolved into COOH, evidence that benzoic acid is really a benzöene derivative, not a phenöene derivative. For other modes of obtaining benzoic acid artificially, *see* p. 396. It may also be produced from hippuric acid (benzamidacetic acid), p. 402. Benzoic acid heated with lime yields benzene :—

$$\underset{\text{Benzoic acid.}}{C_6H_5COOH} + \underset{\text{Calcium oxide.}}{CaO} = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

Benzoic Aldehyde, or *Benzaldehyde*, C_6H_5COH, forms the greater part of oil of bitter almonds (*see* Amygdalin, p. 595). It is a colourless liquid, soluble in 30 parts of water, and in all proportions in ether and alcohol. With acid sulphite of potassium it, like other aldehydes, forms a crystalline compound, $C_6H_5\cdot COH\cdot NaHSO_3$.

Benzoyl Chloride, C_7H_5OCl, results from the action of chlorine on benzaldehyde (formerly termed *benzoyl hydride*, C_7H_5OH) or from the action of pentachloride of phosphorus on benzoic acid (*benzoyl hydrate*, C_7H_5OOH). Benzaldehyde also results from the oxidation of the benzyl alcohol (C_7H_7OH) of balsam of Peru.

The other acids of this series are not very important.

The Hydroxybenzoic Series.

Acids of the Hydroxybenzoic Series, $C_nH_{2n-8}OH\cdot COOH$.—Just as the acids of the lactic series are related to the acetic series, so are the acids of the hydroxybenzoic (or salicylic) series related to the benzoic series.

CH_3COOH Acetic acid.	$CH_2OH\cdot COOH$ Hydroxyacetic or glycollic acid.
C_6H_5COOH Benzoic acid.	$C_6H_4OH\cdot COOH$ Hydroxybenzoic or salicylic acid.

Salicylic or *Hydroxybenzoic Acid*, $C_7H_6O_3$ or $C_6H_4OH\cdot COOH$ (*Acidum Salicylicum*, B.P.). Natural salicylate of methyl is described on p. 485. It also occurs in several species of violet (Mandelin). Salicylic acid may be made by the oxidation of salicylic aldehyde (*vide infra*), or by the action of carbonic acid on phenol or carbolic acid (Kolbe). To accomplish this, the phenol is mixed with caustic soda, forming sodium-phenol or carbolate of sodium, C_6H_5ONa. The sodium-phenol is then saturated with carbonic acid at the ordinary temperature, by which phenylcarbonate of sodium is produced. The latter on being heated in closed vessels is transformed into salicylate of sodium, from which salicylic acid may be obtained by the action of hydrochloric acid, and purification by recrystallization from alcohol. It appears to be identical with the natural acid.

$$\underset{\text{Sodium phenol, or Carbolate of sodium.}}{C_6H_5{\cdot}ONa} + CO_2 = \underset{\text{Phenylcarbonate of sodium.}}{C_6H_5O{\cdot}CO{\cdot}ONa}$$

$$\underset{\text{Phenylcarbonate of sodium.}}{C_6H_5O{\cdot}CO{\cdot}ONa} = \underset{\text{Salicylate of sodium.}}{C_6H_4OH{\cdot}CO{\cdot}ONa}$$

$$\underset{\text{Salicylate of sodium.}}{C_6H_4OH{\cdot}CO{\cdot}ONa} + HCl = \underset{\text{Salicylic acid.}}{C_6H_4OH{\cdot}CO{\cdot}OH} + NaCl$$

Salicylate of Phenyl, $C_6H_4OH{\cdot}CO{\cdot}OC_6H_5$, or *salicylic phenol*, or, shortened, *salol*, is a new antiseptic, antipyretic, antirheumatic remedy. It is white, crystalline, soluble in alcohol, insoluble in water, and of an aromatic odour.

Table showing the Relations between the Benzoic and Hydroxybenzoic Acids.

Benzoic acid	$C_6H_5{\cdot}CO{\cdot}OH$.
Hydroxybenzoic or salicylic acid	$C_6H_4OH{\cdot}CO{\cdot}OH$.
Dihydroxybenzoic acid	$C_6H_3(OH)_2{\cdot}CO{\cdot}OH$.
Trihydroxybenzoic or gallic acid	$C_6H_2(OH)_3{\cdot}CO{\cdot}OH$.

Salicylic acid, like carbolic acid, is a powerful antiseptic, but is free from the taste and smell of carbolic acid. It is only slightly soluble in cold water, but readily soluble in hot water, alcohol, ether, and in aqueous solutions of such alkali-metal salts as borax, phosphate of sodium, or citrate of potassium, which it converts into acid salts with formation of a salicylate. A similar antiseptic *cresotic acid* (hydroxytoluic acid, $C_6H_3OH{\cdot}CH_3{\cdot}COOH$) is similarly obtained from cresol or cresylic acid, $C_6H_4OH{\cdot}CH_3$. Ferric chloride strikes a violet coloration with both salicylic and cresotic acids. Both acids have antipyretic powers. The true salicylates of the alkali-metals, and probably therefore the cresotates, are very feeble antiseptics. Salicylate of sodium (*Sodii Salicylas*, B.P.), $(NaC_7H_5O_3)_2,H_2O$, the old Salicylate of Soda, made by neutralizing salicylic acid with hydrate or carbonate of sodium, forms small, nearly colourless, lamellar crystals, soluble in alcohol, and readily soluble in water. Carbolic acid often containing cresylic acid, commercial salicylic acid may contain cresotic acid. An alcoholic solution of salicylic acid allowed to evaporate spontaneously, exposure to dust being avoided, should leave a white residue free from colour even at the points of the crystals. Salicylic acid yields coloured substances on being nitrated and etherified, etc. *Iodosalicylic acid* and *di-iodosalicylic acid*, $C_7H_5IO_3$ and $C_7H_4I_2O_3$, are used in medicine.

Salicylic Aldehyde, or hydroxybenzoic aldehyde, $C_6H_4OH \cdot COH$ (salicylous acid, hydride of salicyl).—Found in the essential oil of meadow-sweet (*Spirea ulmaria*); also obtained by the oxidation of saligenin (*see* p. 604). It may be artificially formed by the action of chloroform on sodium-phenol.

Preparation.—Mix 10 parts of phenol with 20 parts of sodium hydrate dissolved in 30 parts of water in a flask having an upright condenser, and gradually add 20 parts of chloroform. After heating the flask on a water-bath, until all chloroform has disappeared, add excess of hydrochloric acid, when a red-violet oil will rise to the surface. Pour the contents of the flask into a retort, and pass steam through it till no more aldehyde comes over. The reaction is as follows:—

$$\underset{\text{Sodium phenol.}}{C_6H_5ONa} + 3NaOH + \underset{\text{Chloroform.}}{CHCl_3} = \underset{\text{Sodium salicylic aldhyde.}}{C_6H_4ONa \cdot COH} + 3NaCl + 2H_2O.$$

This, treated with hydrochloric acid, gives:—

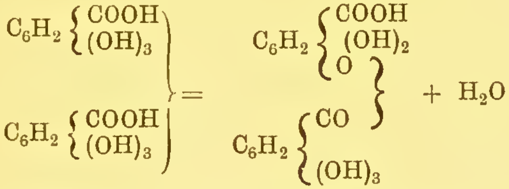
$$\underset{\text{Sodium salicylic aldehyde.}}{C_6H_4ONa \cdot COH} + HCl = \underset{\text{Salicylic aldehyde.}}{C_6H_4(OH)COH} + NaCl.$$

The oil which passes over (orthohydroxybenzoic aldehyde) may be purified from phenol (with which it is always contaminated) by treating with acid sulphite of sodium, which forms a compound with the aldehyde, leaving the phenol which may be removed by dissolving in ether. An isomeric salicylic aldehyde (parahydroxybenzoic aldehyde) is formed with the ortho-aldehyde, and remains dissolved in the water in the retort, from whence it is precipitated on cooling.

Coumarin, $C_9H_6O_2$ (the principle of the Tonka bean), may be obtained by acting on the sodium-derivative of salicylic aldehyde with acetic anhydride and sodium acetate (Perkin).

The Trihydroxybenzoic Series.

Acids of the Series ($C_nH_{2n-10}(OH)_3COOH$). *Gallic Acid*, or trihydroxybenzoic acid, $C_6H_2(OH)_3COOH$ (*see* p. 426). By the elimination of one molecule of water from two molecules of gallic acid, tannic acid is produced.



$$\left.\begin{array}{l} C_6H_2\left\{\begin{array}{l}COOH\\(OH)_3\end{array}\right. \\ \\ C_6H_2\left\{\begin{array}{l}COOH\\(OH)_3\end{array}\right.\end{array}\right\} = \begin{array}{l} C_6H_2\left\{\begin{array}{l}COOH\\(OH)_2\\O\end{array}\right. \\ C_6H_2\left\{\begin{array}{l}CO\\ \\(OH)_3\end{array}\right.\end{array}\!\!\left.\begin{array}{l}\\ \\ \\ \\ \end{array}\right\} + H_2O$$

Gallic Acid. Tannic Acid.

Gallic acid (or tannin, *see* p. 426) by heat yields *pyrogallol* or *pyrogallic acid* and carbonic anhydride.

$$C_6H_2(OH)_3COOH \quad = \quad C_6H_3(OH)_3 \quad + \quad CO_2$$

The Cinnamic Series.

Acids of the Cinnamic Series, $C_nH_{2n-9}COOH$.—Cinnamic acid, C_8H_7COOH, may be obtained from the balsams of tolu, Peru, and storax. It may be made artificially by a process analogous to that by which coumarin is, as just stated, prepared from salicylic aldehyde.

1. *Balsam of Peru* (*Balsamum Peruvianum*, B.P.), an exudation from the trunk of *Myroxylon Pereiræ*, is a mixture of oily matter with about one-quarter or one-third resinous matter, and 6 per cent. of cinnamic acid. The oil, by fractional distillation in an atmosphere of carbonic acid gas and under diminished pressure, furnishes *benzyl-hydrate*, or *benzylic alcohol* ($C_6H_5CH_2OH$), *benzoate of benzyl* ($C_6H_5CO{\cdot}OC_7H_7$), and *cinnamate of benzyl* ($C_8H_7CO{\cdot}OC_7H_7$), or *cinnamein* (Kraut). By action of alcoholic solution of potash it yields benzoate and cinnamate of potassium, and benzylic alcohol; also *cinnamic alcohol* ($C_8H_7CH_2OH$), otherwise known as *peruvine* or *styrone*; it also often holds in solution *metacinnamein* or *styracin* ($C_{18}H_{16}O_2$), isomeric with cinnamic aldehyde (C_8H_7COH). The resin of balsam of Peru seems to result from the action

of moisture on the oil. Any admixture of resin, oil, storax, benzoin, or copaiva, with balsam of Peru is detected by mixing six grains of slaked lime with ten drops of the balsam, when a soft product results if the specimen be pure, but hard, if impure; further, the mixture, on being warmed until volatile matter is expelled and charring commences, gives no fatty odour. 2. *Balsam of Tolu* (*Balsamum Tolutanum*, B.P.) is an exudation from the trunk of *Myroxylon Toluifera;* in composition it closely resembles balsam of Peru, but is more susceptible of resinification. It contains benzoate and cinnamate of benzyl, cinnamic acid, a little benzoic acid (Busse), and about 1 per cent. of a volatile hydrocarbon, *tolene*, $C_{10}H_{16}$. The cinnamic acid crystals may be seen with a lens when a little of the balsam is pressed between two warmed pieces of glass. Old hard balsam of tolu is a convenient source of cinnamic acid, which may be extracted by the same process as that by which benzoic acid is obtained from benzoin—namely, ebullition with alkali, filtration, and precipitation by hydrochloric acid. 3. *Storax* is an oleo-resin obtained from the *Liquidambar orientale.* It contains a volatile oil termed *styrol*, *cinnamene*, or *cinnamol* (C_8H_8)—which possibly (Berthelot) is condensed acetylene, $4C_2H_2$—cinnamic acid, styracin, or cinnamate of cinnamyl ($C_8H_7CO \cdot OC_9H_9$) and a soft and a hard resin. Styrol differs from similar hydrocarbons in being converted into a polymeric solid, termed *metastyrol* or *draconyl*, on heating to about 400° F. For medicinal use, storax (*Styrax Præparatus*, B.P.) is purified by solution in alcohol, filtration, and removal of the alcohol by distillation. By oxidation with red chromate of potassium and sulphuric acid it yields an odour resembling that of essential oil of bitter almonds.

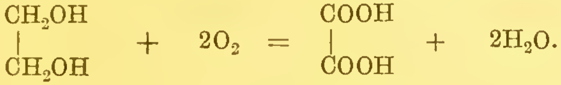
Dibasic Acids.

Dibasic Acids are acids having two carboxyl (COOH) groups in the molecule.

The Succinic Series.

Acids of the Succinic Series, $C_nH_{2n}(COOH)_2$.—These acids may be formed by the oxidation of glycols, or by the action of water and hydrochloric acids on the cyanides of the olefines, obtained by acting on the olefine dibromo-additive derivatives by potassium cyanide.

Oxalic Acid, $C_2O_4H_2$, or $(COOH)_2$, is the first of this series. It may be obtained by oxidizing glycol, $C_2H_4(OH)_2$—



$$\underset{\text{Glycol.}}{\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}} + 2O_2 = \underset{\text{Oxalic Acid.}}{\begin{array}{c} COOH \\ | \\ COOH \end{array}} + 2H_2O.$$

Also by the action of carbonic anhydride on metallic sodium:—

$$\underset{\text{Carbonic anhydride.}}{2CO_2} + \underset{\text{Sodium.}}{Na_2} = \underset{\text{Sodium oxalate.}}{C_2O_4Na_2}$$

For other methods, *see* Oxalic Acid, p. 372.

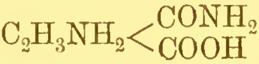
Oxamide, $C_2O_2(NH_2)_2$, the analogue of urea,—carbamide, $CO(NH_2)_2$,—is formed on mixing oxalate of ethyl with ammonia; or by passing cyanogen into aqueous hydrochloric acid $C_2N_2 + 2H_2O = (CONH_2)_2$.

Succinic Acid, $C_2H_4(COOH)_2$. (*See* p. 420.)

The Malic Series.

Acids of the Malic Series, $C_nH_{2n-1}OH(COOH)_2$.—Malic, or hydroxysuccinic acid, $C_2H_3(OH)\ (COOH)_2$, is obtained artificially by acting on bromosuccinic acid, $C_2H_3Br(COOH)_2$, with moist silver oxide, the bromine being replaced by hydroxyl. It is contained in unripe mountain-ash berries, morello cherries, etc. (*See* p. 411.)

Asparagin (amidosuccinamic acid), $C_2H_3NH_2{<}\begin{smallmatrix} CONH_2 \\ COOH \end{smallmatrix}$ (*See* p. 412.)



The Tartaric Series.

Acids of the Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$.—*Tartaric Acid* (dihydroxysuccinic acid), $C_2H_2(OH)_2(COOH)_2$, may be obtained by oxidizing erythrite, $C_2H_2(OH)_2(CH_2OH)_2$. (*See* p. 553.) For other modes of formation, *see* p. 374. There are four isomeric tartaric acids, differing by their action on a ray of polarized light.

The Phthalic Series.

Acids of the Phthalic Series, $C_nH_{2n-8}\ (COOH)_2$. *Phthalic Acid*, $C_6H_4(COOH)_2$, is obtained by the oxidation of napthalene and napthalene tetrachloride, or a mixture of benzene and benzoic acid. By distillation it forms phthalic anhydride, $C_8H_4O_3$, and this when heated with phenol and sulphuric acid yields *phenolphthalein* (B.P.), a light yellow crystalline powder, which when dissolved in alcohol is used in alkalimetry for its property of turning brilliant red with the slightest excess of alkali. There are three phthalic acids, phthalic acid or orthophthalic acid, $C_6H_4 \cdot COOH \cdot COOH_{(o)}$; isophthalic acid or metaphthalic acid, $C_6H_4 \cdot COOH \cdot COOH_{(m)}$, and terephthalic acid or paraphthalic acid, $C_6H_4 \cdot COOH \cdot COOH_{(p)}$. (*See* p. 542.)

TRIBASIC ACIDS.

Tribasic Acids, having three carboxyl (COOH) groups in the molecule. *Tricarballylic Acid*, or propane-tricarboxylic acid, $C_3H_5(COOH)_3$, is the first of these series; its hydroxy-derivative, is *citric acid*, $C_3H_4(OH)\ (COOH)_3$, (hydroxy-propane-tricarboxylic acid), found in fruits. It has already been described (*see* p. 380).

OTHER POLYBASIC ACIDS.

Tetrabasic acids—as pyromellitic acid, $C_6H_2(COOH)_4$—and *hexabasic* acids—as mellitic acid, $C_6(COOH)_6$—are known.

QUESTIONS AND EXERCISES.

Give general methods for the formation of aldehydes and acids.—How is acetaldehyde prepared?—Describe the reactions that occur in the manufacture of chloral and chloral hydrate.—What is the nature of the action of alkalies on chloral hydrate?—Mention the characters of pure and impure chloral hydrate.—What relation has valerianic acid to amylic alcohol?—Give the relations between the acetic and lactic series of acids.—To what series do the following acids belong: —Oleic, butyric, oxalic, and citric?—How is benzoic acid prepared? Give the differences between balsam of Peru, tolu, and gum benzoin.—How is oil of bitter almonds prepared? and how can it be distinguished from so-called artificial oil of bitter almonds?—Give artificial methods of preparing salicylic aldehyde and acid.—Give systematic names of tartaric, succinic, carbonic, salicylic, and citric acids.

TABLE SHOWING THE RELATIONS BETWEEN THE ACIDS OF THE ACETIC SERIES AND THE DIBASIC ACIDS.

Acids of the Acetic Series, $C_nH_{2n+1}COOH$.	Acids of the Succinic Series $C_nH_{2n}(COOH)_2$.	Acids of the Hydroxysuccinic or Malic Series, $C_nH_{2n-1}(OH)(COOH)_2$.	Acids of the Dihydroxysuccinic or Tartaric Series, $C_nH_{2n-2}(OH)_2(COOH)_2$.
Formic, $H{\cdot}CO{\cdot}OH$	Oxalic, $COOH{\cdot}COOH$	—	—
Acetic, $CH_3{\cdot}CO{\cdot}OH$	Malonic, $CH_2(CO{\cdot}OH)_2$	Tartronic (oxymalonic), $CH{\cdot}OH{\cdot}(COOH)_2$	Mesoxalic, $C(OH)_2(COOH)_2$
Propylic, $C_2H_5{\cdot}CO{\cdot}OH$	Succinic, $C_2H_4(CO{\cdot}OH)_2$	Malic (oxysuccinic), $C_2H_3{\cdot}OH{\cdot}(COOH)_2$	Tartaric (or dioxysuccinic), $C_2H_2(OH)_2(COOH)_2$
Tetrylic, $C_3H_7{\cdot}CO{\cdot}OH$	Pyro artaric, $C_3H_6(CO{\cdot}OH)_2$	Glutanic, $C_3H_5{\cdot}OH{\cdot}(COOH)_2$	Homotartaric $C_3H_4(OH)_2(COOH)_2$

KETONES.

Just as primary alcohols on losing hydrogen yield aldehydes, so secondary alcohols (*see* p. 521) on losing hydrogen yield ketones:—

$$C_nH_{2n+1}CH_2OH \quad - \quad H_2 \quad = \quad C_nH_{2n+1}\,COH$$
$$(C_nH_{2n+1})_2CHOH \quad - \quad H_2 \quad = \quad (C_nH_{2n+1})_2CO$$

Like aldehydes, ketones are converted by nascent hydrogen into the corresponding alcohols. Like aldehydes, ketones form crystalline compounds with acid sulphites. While, however, aldehydes by oxidation yield corresponding acids, ketones break up and yield acids whose molecules have a smaller number of carbon atoms.

Acetone, C_3H_6O, or *dimethyl-ketone*, $(CH_3)_2CO$ or $CH_3{\cdot}CO{\cdot}CH_3$, the original and best known of the class, may be obtained by strongly heating acetate of calcium, carbonate remaining. The calcium salts of other fatty radicals split up in a similar manner (hence perhaps the name—from κέω, *keō*, I split, and the original *acetone*), yielding other ketones, as propione, butyrone, valerone, etc. The mixed calcium salts give corresponding ketones. Thus acetate and caprate yield methy-nonyl ketone, $CH_3-CO-C_9H_{19}$, the chief natural constituent of oil of rue. *Acetophenone* or *phenylmethyl ketone*, $C_6H_5{\cdot}CO{\cdot}CH_3$ is known as *hypnone.*

$$\underset{\text{Acetate of calcium.}}{(CH_3COO)_2\,Ca} \quad = \quad \underset{\text{Acetone.}}{(CH_3)_2\,CO} \quad + \quad \underset{\text{Carbonate of calcium.}}{Ca\,CO_3}$$

Note.—There are many organic substances the composition of which has been established, and the characters of which are definite, whether basic, acid, or neutral, but whose constitution is still so questionable that they cannot yet be classified with the hydrocarbons and derivatives of hydrocarbons. These are the glucosides, alkaloids, albumenoids, certain colouring matters, etc. They are described in the following pages.

THE GLUCOSIDES.

Source.—The glucosides are certain proximate vegetable principles which, by ebullition with dilute acid, or other method of decomposition, take up the elements of water and yield glucose, accompanied by a second substance, which differs in each case according to the body operated on. Several of the glucosides which are of pharmaceutical interest will now be considered. Tannin has also been said to be a glucoside; it has been described among the acids.

There are indications that all glucosides may be regenerated from the bodies into which they are thus converted.

Note on Nomenclature.—The first syllable of the names of glucosides and neutral principles generally are commonly given in allusion to origin; the last syllable is *in*, which sufficiently distinguishes them as a class.

ABSINTHIN ($C_{15}H_{10}O_4$), the bitter principle of *Artemisia Absinthium*, or *wormwood*, yields, when boiled with acids, glucose, volatile oil and a resin of the aromatic series. (The liqueur termed *absinthe* is spirit of wine flavoured with natural oil of wormwood, coloured by chlorophyll, and slightly sweetened.)

AMYGDALIN ($C_{20}H_{27}NO_{11},3H_2O$). This body, obtained by Robiquet and Boutron-Charlard in 1830, was the first discovered glucoside (Liebig and Wöhler, 1837). It is a white crystalline substance, existing in the bitter (*Amygdala Amara*, B.P.) but not in the sweet almond (*Amygdala Dulcis*, B.P.). About 2 per cent. is readily extracted by strong alcohol from the cake left when the fixed oil has been expressed from bitter almonds. From the concentrated alcoholic solution ether precipitates the amygdalin.

Make an emulsion of two or three sweet almonds by bruising and rubbing them with water, and notice that it has no odour of essential oil of bitter almonds; add a grain or two of amygdalin: an odour of essential oil of bitter almonds is at once developed. Bruise two or three bitter almonds and rub with water: the volatile oil is again developed.

The source of the benzaldehyde, or essential oil of bitter almonds, in these reactions, is the amygdalin, which, under the influence of *synaptase* or *emulsin* (a nitrogenous, casein-like ferment existing in bitter and sweet almonds), splits up into essential oil, hydrocyanic acid, and glucose:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Benzaldehyde.}}{C_6H_5COH} + \underset{\substack{\text{Hydro-}\\\text{cyanic acid.}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

As each molecule of amygdalin yields one of hydrocyanic acid, a simple calculation shows that 17 grains (mixed with emulsion of sweet almonds) will be required to form one grain of real hydrocyanic acid, a quantity equivalent to 50 minims of the diluted hydrocyanic acid of the British Pharmacopœia. The hydrocyanic acid is probably in chemical combination with the oil, to the extent of about 5 per cent. According to Linde, the occurrence of the benzaldehyde is preceded by the formation of benzaldehydcyanhydrin ($C_6H_5CH(OH)CN$). The emulsin and amygdalin occur in different parts of the bitter almond.

Test.—The reaction between synaptase and amygdalin is applicable as a test of the presence of one by the addition of the other, even when mixed with much organic matter.

Jacobsen obtains true benzaldehyde artificially from benzodichloride (dichloromethylbenzene, $C_6H_5CHCl_2$), one of the dichlorotoluenes, by heating with glacial acetic acid and chloride of zinc with a little water.

Cherry Laurel Water (*Aqua Laurocerasi*, B.P., by distillation with water from *Laurocerasi Folia*, B.P.) contains hydrocyanic acid derived from a reaction similar to, indeed probably identical with, that described above, for bitter almond oil is simultaneously produced. But the proportion of amygdalin or analogous body in cherry-laurel leaves is most variable; hence normally the strength of the water is highly uncertain. The British Pharmacopœia, however, directs that it shall contain 0·1 per cent. of real hydrocyanic acid, it being strengthened by the addition of hydrocyanic acid, or, if necessary, diluted by the addition of distilled water, until it has the prescribed strength.

Linseed yields a glucoside, *linamarin*, related to amygdalin, for it yields glucose and hydrocyanic acid on hydrolysis.

Cortex Pruni Serotinæ.—The recently dried Wild Cherry Bark also furnishes by distillation an essential oil and hydrocyanic acid. Quince-seeds also (*Pyrus Cydonia*). The above Wild Black Cherry (*Prunus Virginiana*, U.S.P), collected in autumn, contains amygdalin.

Caution.—Essential oil of almonds is of course highly poisonous. The purified oil or benzaldehyde is almost innocuous; it is obtained on distilling the crude oil with milk of lime and ferrous chloride, and drying the product by shaking with fused chloride of calcium. The so-called "artificial oil of bitter almonds" or "nitrobenzol" [$C_6H_5NO_2$], when taken in quantity, has been known to produce death. The presence of nitrobenzol in oil of bitter almonds is detected by adding a little of the oil to a mixture of zinc and diluted sulphuric acid, shaking well, setting aside for an hour or two, filtering off the clear liquid, and adding a little chlorate of potassium; a violet colour (actual mauve) is produced. The reaction is due to the formation of phenylamine or aniline (*see* p. 514). Or the specimen may be shaken with bisulphite of sodium to fix the benzaldehyde (for all such aldehydes form a compound with bisulphite of sodium), and then with ether, which dissolves out, and on evaporation will yield, the nitrobenzol.

ARBUTIN ($C_{12}H_{16}O_7$) and *methyl-arbutin* ($C_{13}H_{18}O_7$) is contained in the leaves of *Arctostaphylos Uva Ursi*, *Chimaphila umbellata* and many ericaceous plants. It is a bitter neutral body occurring in acicular crystals, and resolvable by acids into *hydroquinone* ($C_6H_6O_2$) and glucose, and by gentle oxidation into *quinone* ($C_6H_4O_2$) and formic acid. *Ericolin* ($C_{34}H_{56}O_{21}$) is another bitter glucoside in bearberry-leaves.

CATHARTIC ACID.—"The glucoside acid that now is known to confer on the Senna of Alexandria (*Senna Alexandrina*, B.P.) and of Tinnevelly (*Senna Indica*, B.P.) its purgative property has been named by its discoverers (Dragendorff and Kubly) cathartic acid. Its formula has been stated as $C_{180}H_{192}N_4SO_{82}$ (but A. Gensz more recently states it to be $C_{30}H_{36}NO_{15}$). It is insoluble (?) in water, strong alcohol, and ether, but enters readily into either solution when combined with alkaline and earthy bases, in which state it exists in senna. Its ammonium salts give brownish flocculent precipitates with salts of silver, tin, mercury, copper, and lead. Antimonial salts, tannin, and yellow and red prussiates have no effect upon it. Alkalies, aided by heat, act destructively upon it. Boiled with a mineral acid, it splits into a peculiar kind of glucose and an acid that has been named cathartogenic; its formula is said to be $C_{132}H_{116}N_4SO_{44}$. The natural cathartate occurring in senna is prepared by partially precipitating by strong spirit a watery infusion of senna, concentrated to a syrupy state by evaporation *in vacuo*. The filtrate is now treated with a much larger bulk of absolute alcohol, and the precipitate thus obtained is purified by repeated solution in water and precipitation by alcohol. To obtain the pure acid, advantage is taken of its colloidal properties; the crude cathartate is dissolved in moderately strong hydrochloric acid, and subjected to dialysis on a diaphragm of parchment paper. The minimum dose of this pure acid was found to be about 1½ grains, which caused several stools with decided griping."

"The cathartic combinations that I have made are, the cathartate of ammonium, prepared from cathartate of lead by my original process, and the mixed cathartates, prepared according to Dragendorff's method as modified by myself. Of the former nearly pure salt, I have found 3¾ grains to purge fairly as to amount, but slowly as to time, and with considerable griping. Of the latter 7½ grains purged violently with much griping and sickness, which continued through the greater part of the day. It obviously would be improper to combine senna with any of its metallic precipitants, should such be desired, which is not likely. It is here satisfactory to observe that the cathartate of magnesium is soluble, and that the old-fashioned black draught agrees with new-fashioned science" (Groves).

Buckthorn Juice (*Rhamni Succus*, B.P., 1867) owes its cathartic properties to a substance apparently identical with cathartic acid.

COLOCYNTHIN ($C_{56}H_{84}O_{23}$?).—This substance is the active bitter and purgative principle of colocynth-fruit (*Colocynthidis Pulpa*, B.P).: it is soluble in water and alcohol, but not in ether. By ebullition with acids it furnishes glucose and a resinoid body.

CONVOLVULIN.—*See* JALAPIN.

COTOIN ($C_{22}H_{18}O_6$) appears to be the chief active principle of Coto bark, a Bolivian remedy for diarrhœa., A similar bark, *false coto*, or *paracoto*, contains *paracotoim*, $C_{19}H_{12}O_6$, and *hydrocotoin*, $C_{15}H_{14}O_4$.

DAPHNIN ($C_{31}H_{34}O_{19}$) is the crystalline glucoside of the bark of *Daphne Mezereum* (*Mezerei Cortex*, B.P.). Boiled with dilute acids, it yields *daphnetin* ($C_{19}H_{14}O_9$) and glucose. The acrid principle of mezereon is resinoid.

DIGITALIN ($C_{27}H_{45}O_{15}$, Kosmann; $C_5H_8O_2$ Schmiedeberg). —This is an active principle of the Foxglove, *Digitalis purpurea*. On boiling a grain of digitalin with diluted sulphuric acid for some time, flocks of *digitaliretin* ($C_{15}H_{25}O_5$) separate, and glucose may be detected in the liquid.

$$\underset{\text{Digitalin.}}{C_{27}H_{45}O_{15}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Digitaliretin.}}{C_{15}H_{25}O_5} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Properties.—Digitalin occurs "in porous mammillated masses or small scales, white, inodorous, and intensely bitter, readily soluble in spirit, but almost insoluble in water and in pure ether; dissolves in acids, but does not form with them neutral compounds; its solution in hydrochloric acid is of a faint yellow colour, but rapidly becomes green. It leaves no residue when burned with free access of air. It powerfully irritates the nostrils, and is an active poison," B.P. 1867. According to Pettenkofer, "an intense red colour is produced if a trace of digitalin dissolved in water is mixed with a weak aqueous solution of inspissated bile and sufficient oil of vitriol added to raise the temperature to 158° F." Moistened with sulphuric acid and the liquid exposed to the vapour of bromine, a violet colour is produced.

Process.—The process for the preparation of digitalin consists in dissolving the glucoside out of the digitalis-leaf (*Digitalis Folia*, B.P.) by alcohol, recovering the alcohol by distillation, dissolving the residue in water by the help of a small quantity of acetic acid, removing much of the colour from the solution by animal charcoal, neutralizing most of the acetic acid by ammonia, precipitating the digitalin by tannic acid (with which it forms an insoluble compound), washing the precipitate, rubbing and heating it with spirit and oxide of lead (which removes the acid in the form of insoluble tannate of lead), again decolourizing by animal charcoal, evaporating to dryness, washing out impurities still remaining by ether, and drying the residual digitalin. In this form digitalin is uncrystallizable and somewhat indefinite.

Pure Digitalin (?).—On treating commercial digitalin with chloroform an inert substance remains undissolved. The solution yields pure digitalin on evaporation; it may be crystallized from spirit in radiating needles (Nativelle). The therapeutic effect of the pure substance is identical with that of the preparations of digitalis, but more constant in its action, and, of course, intensely powerful.

Digitoxin ($C_{31}H_{33}O_7$), ($C_{31}H_{32}O_7$, Dragendorff) is a highly poisonous substance extracted from Foxglove by Schmiedeberg. The same chemist regards commercial digitalin from foxglove seeds as composed of varying proportions of three glucosides, namely, pure active *digitalin* ($C_5H_8O_2$), *digitonin* ($C_{31}H_{52}O_{17}$) (closely allied to saponin), and *digitalein*, with inactive digitalin or *digitin*. Kiliani says that Schmiedeberg's digitalein is a mixture, and that his "digitalin," which is a pure but uncrystallisable glucoside $C_5H_8O_2$, is the true active principle. *Digitonin*, $C_{27}H_{46}O_{14}$, (Kiliani) yields on hydrolysis *digitogenin* $C_{15}H_{24}O_3$, galactose $C_6H_{12}O_6$, and dextrose, $C_6H_{12}O_6$.

ELATERIN ($C_{20}H_{28}O_5$).—Boil elaterium (*Elaterium*, B.P.), the dried sediment from the juice of the squirting-cucumber fruit (*Ecballii Fructus*, B.P.), with chloroform, filter, evaporate, wash with ether the precipitated elaterin, recrystallize it from chloroform and again wash the crystals with ether. The product, the official *Elaterinum* B.P., occurs in small hexagonal plates or prisms.

Elaterin is probably not a true glucoside. It does not always respond to the test for glucose after boiling with acids; and when it does, the reaction is possibly due to *prophetin*, a glucoside stated by Walz to be present in elaterium.

Elaterin is the active principle of the so-called elaterium. Elaterium occurs in light friable greenish-grey cakes. Good specimens of this drug should yield not less than 20 per cent. of elaterin by the above process.

Test.—A little is placed in a watch-glass with a drop of liquefied carbolic acid, and then two drops of strong sulphuric acid: a carmine colour is developed. (Lindo.)

FRANGULIN, $C_{21}H_{20}O_9$, is a glucoside found in the bark of *Rhamnus frangula.* It is decomposed on hydrolysis into *emodin*, $C_{15}H_{10}O_5$, and an unfermentable sugar, *rhamnose* $C_6H_{12}O_5$.

GENTIOPICRIN, or GENTIAN-BITTER ($C_{20}H_{30}O_{12}$), the neutral crystalline principle of the root of *Gentiana lutea* (*Gentianæ Radix*, B.P.). It is soluble in water and weak spirit. Alkalies decompose it. Dilute acids convert it into *gentiogenin* and glucose. Gentian root also contains a variety of tannin and a crystalline acid ($HC_{14}H_9O_5$) termed *gentianic*, or *gentisic acid*, or *gentisin.* Fused potash, etc., gives with the latter an acid ($C_7H_6O_4$), which has also, unfortunately, been called gentisic acid.

GLYCYRRHIZIN ($C_{24}H_{36}O_9$, Gorup-Besanez) or *Glycyrrhizic Acid* ($C_{44}H_{63}NO_{18}$, Habermann).—Liquorice-root (*Glycyrrhizæ Radix*, B.P.), in addition to uncrystallizable sugar, contains 3 or 4 per cent. of a sweet substance, *glycyrrhizin*, which, when boiled with hydrochloric acid or diluted sulphuric acid, yields a resinoid bitter body, *glycyrretin*, and an uncrystallizable sugar resembling glucose. Glycyrrhizin is only slightly soluble in cold water, hence is almost wholly excluded from the official evaporated infusion (*Extractum Glycyrrhizæ*, B.P., and *Extractum Glycyrrhizæ Liquidum*, B.P.), but is present in considerable quantity in the evaporated decoction (*Stick Liquorice*, *Spanish Liquorice*, or *Solazzi Juice*). It is soluble in ammoniacal water. The tropical substitute for liquorice is the root of *Abrus precatorius*, or *Indian Liquorice* (*Abri Radix*, P.I.), the *kunch* or *gunj* of Bengal, the *ratti* of Hindustan, and the *jequirity* or *jequerity* of Brazil, which also contains glucose and glycyrrhizin. The seeds yield by maceration a substance which acts as a poison when injected into the blood, but not when swallowed. Warden and Waddell regard the active principle as an albumenoid and term it *abrin*. Bruylants and Venneman consider it to be a product of germination, and call it *jequeritin*. Bechamp and Dujardin regard the latter as a mixture of legumin and *jequerityzymase*. Glycyrrhizin has considerable power of disguising nauseous flavours. Roussin refers the sweet taste of liquorice not to pure glycyrrhizin but to a combination of glycyrrhizin with alkalies, and states that ammoniacal glycyrrhizin has exactly the sweetness of liquorice-root. The formula of this *glycyrrhizate of ammonium* is said by Habermann to be $(NH_4)_3C_{44}H_{60}NO_{18}$. Sestini finds that the glycyrrhizin of liquorice-root is chiefly glycyrrhizate of calcium.

GUAIACIN.—Resin of guaiacum (*Guaiaci Resina*, B.P.), an exudation from the wood (*Guaiaci Lignum*, B.P.) of *Guaiacum officinale*, is probably a mixture of several substances, among which are *guaiaretic*, or *guaiaretinic acid* ($C_{20}H_{26}O_4$, Hlasiwetz), *guaiaconic acid* ($C_{38}H_{40}O_{10}$, Hadelich), and *guaiacin*, a glucoside. On boiling guaiacum-resin with diluted sulphuric acid for some time, glucose is found in the liquid, a green resinous substance (*guaiaretin*) remaining insoluble (Kosmann). Most oxidizing agents, and even atmospheric air, especially under the influence of certain organic substances, produce a blue, then green, and finally a brown colour when brought into contact with an alcoholic solution of guaiacum resin.

These effects are said to be due to three stages of oxidation (Jonas). They may be observed on adding the solution to the inner surface of a paring of a raw potato.

HELLEBORIN ($C_{36}H_{42}O_6$) and HELLEBOREIN ($C_{26}H_{44}O_{15}$) are crystalline glucosides occurring in the roots of Black Hellebore (*Helleborus niger*), or Christmas rose, and Green Hellebore (*H. viridis*), ranunculaceous herbs.

JALAPIN ($C_{31}H_{50}O_{16}$) and CONVOLVULIN ($C_{34}H_{56}O_{16}$).—According to Keyser and Meyer, jalap-resin contains two distinct substances—convolvulin, chiefly obtained from Mexican male jalap (*Ipomœa Orizabensis*), and jalapin, most largely contained in the true jalap (*Ipomœa purga*); the former is soluble in ether, the latter insoluble. Boil jalap-resin with diluted sulphuric acid for some time, and filter; a substance, which is probably a mixture of *jalapinol* ($C_{13}H_{24}O_3$) and *convolvulinol* ($C_{16}H_{30}O_3$), separates; glucose may be detected in the clear liquid. (It is to be regretted that the authors transpose these names, terming the old well-known jalapin convolvulin.)

$$\underset{\text{Jalapin.}}{C_{31}H_{50}O_{16}} + \underset{\text{Water.}}{5H_2O} = \underset{\text{Jalapinol.}}{C_{13}H_{24}O_3} + \underset{\text{Glucose.}}{3C_6H_{12}O_6}$$

Jalapic Acid.—This is contained in the portion of jalap resin soluble in ether. It may also be obtained from jalapin by ebullition with alkalies:—

$$\underset{\text{Jalapin.}}{2C_{31}H_{50}O_{16}} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Jalapic acid.}}{C_{62}H_{106}O_{35}}$$

Jalap-resin (*Jalapæ Resina*, B.P.) is obtained by digesting and percolating jalap tubercles (*Jalapa*, B.P.) with spirit of wine, adding a little water, distilling off the spirit, pouring away the aqueous portion, which contains much saccharine matter, and washing and drying the residual resin. Jalap thoroughly exhausted by this process should furnish, according to the British Pharmacopœia, not less than ten per cent. of resin, of which resin (*Jalapæ Resina*, B.P.) not more than one-tenth should be soluble in ether; a test which excludes the so-called "Tampico" jalap, the resin of which is soluble in ether. The tincture of jalap is sometimes decolorized by animal charcoal, and the evaporated product sold as "jalapin."

Jalap-resin is insoluble in oil of turpentine; common resin, or rosin, soluble. If the presence of the latter is suspected, the specimen should be powdered, digested in turpentine, the mixture filtered, and the filtrate evaporated; no residue, or not more than yielded by the turpentine itself, should be obtained.

Tampico Jalap, from *Ipomœa simulans*, yields a resin which apparently is chiefly convolvulin, but sometimes contains jalapin; for a sample obtained by Hanbury was entirely soluble in ether, and another extracted by Umney was almost wholly soluble, while Evans purified some, half only of which was soluble.

The *Kaladana resin* or *Pharbitisin* of India (from *Pharbitis Nil*, P.I.), is a cathartic analagous to, if not identical with, resin of Jalap.

LOGANIN, $C_{25}H_{34}O_{14}$, is a glucoside obtained from the pulp of the fruit and from the seeds of *Strychnos Nux vomica*, Loganiaceæ, by Dunstan and Short. Boiled with dilute sulphuric acid, it yields glucose and *loganetin*.

OUABAIN ($C_{30}H_{46}O_{12}$, Arnaud, or $C_{30}H_{52}O_{14}$) is a very poisonous glucoside resembling strophanthin found in arrow poisons prepared from the wood of an *acokanthera* and in the wood itself.

PICROTOXIN (*Picrotoxinum*, B.P.) is a crystalline bitter poisonous principle (πικρὸς, *picros*, bitter, and τοξικὸν, *toxicon*, poison) occurring in *Cocculus Indicus*, the dried fruits of *Anamirta paniculata*. Ludwig regarded it as a glucoside; but its constitution is not yet satisfactorily ascertained. Barth and Kretschy state that the so-called picrotoxin may be separated into *picrotoxin* proper ($C_{15}H_{16}O_6,H_2O$), which is bitter and poisonous; *picrotin* ($C_{25}H_{30}O_{12}+nH_2O$), which is bitter but not poisonous; and *anamirtin* ($C_{19}H_{24}O_{10}$), which is neither bitter nor poisonous. Schmidt asserts that the original picrotoxin is definite, and has the formula $C_{30}H_{34}O_{13}$, but that some solvents decompose it into *picrotoxinin*, $C_{15}H_{16}O_6$, which is poisonous, and *picrotin*, $C_{15}H_{18}O_7$, which is not poisonous.

QUASSIN ($C_{10}H_{12}O_8$, Wiggers; or $C_{31}H_{42}O_9$, Christensen), obtained from *Quassiæ Lignum*, B.P., is said to be a glucoside; but Oliveri and Denaro question the statement, and find quassin to have the formula $C_{32}H_{44}O_{10}$.

SAFFRANIN, *vide* Index.

SALICIN ($C_{13}H_{18}O_7$).—This substance (*Salicinum*, B.P.) is contained in and easily extracted from the bark of willow and of other species of *Salix* and of *Populus*. It occurs in white, shining, bitter crystals, soluble in twenty-eight parts of water or sixty-five of spirit at common temperatures.

Tests.—1. To a small portion of salicin placed on a white plate or dish, add a drop of strong sulphuric acid; a deep red colour is produced.

2. Boil salicin with diluted sulphuric acid for some time; it is converted into *saligenin* or *saligenol* ($C_7H_8O_2$) and glucose. Test for the latter by the copper test.

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Saligenol.}}{C_6H_4(OH)CH_2OH} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

3. To another portion of the liquid, carefully neutralized, add a persalt of iron: a purplish-blue colour is sometimes produced, due to the reaction of the saligenin and the ferric salt. The saligenin is, however, so rapidly decomposed by acids into *saliretin* (C_7H_6O) and water, that this reaction is almost valueless as a test. The saligenin may, however, be obtained by action of synaptase on salicin.

4. Heat a mixture of about 1 part of salicin, 1 of red chromate of potassium, $1\frac{1}{2}$ of sulphuric acid, and 20 of water in a test-tube; a fragrant characteristic odour is evolved, due to the formation of salicylic aldehyde ($C_6H_4OH{\cdot}COH$), an essential oil identical with that existing in meadow-sweet (*Spiræa Ulmaria*) and in heliotrope.

$$\underset{\text{Saligenol.}}{C_6H_4OH{\cdot}CH_2OH} + \underset{\text{Nascent oxygen.}}{O} = \underset{\text{Salicylic aldehyde.}}{C_6H_4{\cdot}OH{\cdot}COH} + \underset{\text{Water.}}{H_2O}$$

SANTONIN ($C_{15}H_{18}O_3$).—This substance is, apparently, the anhydride or, rather, lactone,* of a weak acid (Hesse) insoluble in ammonia, but forming a soluble calcium salt. Indeed, by boiling santonin for twelve hours with baryta water, Cannizarro has obtained a salt from which hydrochloric acid separates *santonic acid* ($C_{15}H_{20}O_4$). From a solution of santonate of calcium the santonin is precipitated by acids. Boiled for some time with diluted sulphuric acid, it yields 87 per cent. of an insoluble resinous substance (*santoniretin*) and glucose (Kosmann). Santonin (*Santoninum*, B.P.) is official in the British Pharmacopœia; it is soluble in an aqueous solution of twice its weight of carbonate of sodium. Possibly (Berthelot) santonin resembles carbolic acid,—in other words, is a phenol, $C_{15}H_{15}3OH$. Its glucosidic character is questionable.

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* The hydroxyacids losing water furnish *lactones*. Aromatic compounds containing NH_2 in the ortho position and losing water by the oxidation and removal of one or two atoms of that hydrogen furnish bodies which may be distinguished as *lactams* and *lactims*.

Process.—The process for its preparation consists in boiling santonica (the dried unexpanded flower-heads or capitula of *Artemisia maritima*) with milk of lime (whereby santonate of calcium is formed), straining, precipitating the santonin or santonic acid by hydrochloric acid, washing with ammonia to remove resin, dissolving in spirit and digesting with animal charcoal to get rid of colouring-matter, setting the spirituous solution aside to deposit crystals of santonin, and purifying by recrystallization from spirit (Mialhe).

Test.—To highly diluted solution of perchloride of iron add an equal bulk of concentrated sulphuric acid. To this reagent add the santonin, or powder or substance suspected to be santonin, and cautiously apply heat. A red, purple, and finally violet colour is produced (Lindo). Santonin added to warm alcoholic solution of potash yields a violet-red colour.

SAPONIN ($C_{32}H_{52}O_{17},H_2O$) is a peculiar glucoside occurring in Soapwort, the root of the common Pink, and many other plants; its solution in water, even though very dilute, froths like a solution of soap. Heated with dilute acids it yields sugar and *saponetin* $C_{40}H_{66}O_{15}$ or *sapogenol*, $C_{14}H_{22}O_2$ (Hesse). Pereira considered *smilacin* (*salseparin* or *parallin*), one of the principles of the supposed activity of Sarsaparilla (*Sarzæ Radix*, B.P.), to be closely allied to, if not identical with, saponin. According to Klunge ("Pharmacographia"), parallin, by action of acids, yields *parigenin*. The aqueous solutions of parallin froth when shaken. Von Schultz states that sarsaparilla contains three homologous glucosides analogous to saponin, namely, sarsaparill-saponin ($C_{20}H_{32}O_{10}$), sarsasaponin ($C_{22}H_{36}O_{10}$) and parallin ($C_{26}H_{44}O_{10}$).

Saponin is also met with in the root of *Polygala Senega* (*Senegæ Radix*, B.P.), though the active principle of senega is said to reside in *polygalic acid*, probably a glucosidic derivative of saponin.

Saponin is readily obtained from the bark of *Quillaja saponaria*, or *soap-bark* (*Quillaja*, U.S.P.), by boiling the aqueous extract in alcohol and filtering while hot. Flocks of saponin separate on cooling. It is a white, non-crystalline, friable powder.

The alleged toxic properties of commercial saponin are said by Kobert to be due to *sapotoxin* and *quillaic acid*.

SCAMMONIN ($C_{34}H_{56}O_{16}$).—Boil resin of scammony (*Scammoniæ Resina*, B.P.) with diluted sulphuric acid for some time; glucose may then be detected in the liquid, a resinous acid termed *scammoniol* ($C_{14}H_{13}O_3$?) being produced at the same time.

Natural scammony (*Scammonium*, B.P.) is an oxudation from incisions in the living root (*Scammoniæ Radix*, B.P.) of *Convolvulus Scammonia*. It contains from 10 to 20 per cent. of gum, and, therefore, when rubbed up with water, gives an emulsion. "Ether removes about 75 per cent. of resin" (B.P.). The official resin of scammony contains no gum, and therefore gives no emulsion when rubbed up with water. It is made by digesting the root in spirit, adding water, distilling off the alcohol, and washing the residual resin with hot water till free from gum. There seems to be little or no chemical difference between the extracted resin and the resin of the exuded scammony.

Resin of scammony is soluble in all proportions of ether. Spirgatis states that it is identical with the resin of Mexican Male Jalap, which also is soluble in ether. Sulphuric acid slowly reddens it. It is said to be liable to adulteration with resin of true jalap, guaiacum-resin, and common rosin. Resin of true jalap is insoluble in ether, guaiacum-resin is distinguished by the colour-tests mentioned under GUAIACIN, and rosin by the action of sulphuric acid.

SCILLITIN.—Schroff, and, afterwards, Riche and Remont, believed the bitter principle of the squill-bulb (*Scilla*, B.P.) to be a glucoside. Merck has extracted substances which he has termed *scillipicrin*, *scillitoxin*, and *scillin*. Schmiedeberg has given the name of *sinestrin* to a squill principle. But no definite crystalline principle has yet been obtained. Squill contains a large quantity of mucilage.

The bulbous root of *Crinum Asiaticum* is official in the Pharmacopœia of India (*Crini Radix*, P.I.) as a substitute for squill. It has not been chemically investigated.

STROPHANTHIN ($C_{20}H_{34}O_{10}$; Arnaud, $C_{31}H_{48}O_{12}$).—According to Fraser, this is the active principle of strophanthus seed (*Strophanthus hispidus*, *var. Kombé*) and is a glucoside. He obtained it in crystals. Acids convert it into glucose and crystalline *strophanthidin*. Phosphomolybdic acid produces in solutions of strophanthin a bright bluish-green colour. Helbing states that its aqueous solution yields, with a trace of solution of perchloride of iron and a little strong sulphuric acid, a reddish-brown precipitate which after an hour or two turns green. Sulphuric acid colours strophanthin dark green, changing to reddish brown. Recent researches indicate that strophanthin is only one of the active principles of the different species of strophanthus. Strophantus is official, *Strophanthus*, B.P., yielding *Tinctura Strophanthi*, B.P.

QUESTIONS AND EXERCISES.

Define glucosides, and mention those of pharmaceutical interest.—Draw out an equation illustrative of the development of oil of bitter almonds.—How much pure amygdalin will yield one grain of real hydrocyanic acid?—To what does cherry-laurel water owe its activity?—Mention the active principle of senna.—By what process is the glucoside of the purple foxglove prepared?—State the circumstances under which guaiacum-resin and jalap-resin yield glucose.—Mention a test for guaiacum-resin.—How may the adulteration of jalap-resin by rosin be detected?—Enumerate the tests for salicin.—How is santonin officially prepared?—Name sources of saponin.—What is the difference between scammony and resin of scammony?—How would you detect resins of turpentine, guaiacum, or jalap, in resin of scammony?

BITTER OR TONIC SUBSTANCES, ETC.

The following articles, employed medicinally in such forms as Decoction, Extract, Infusion, Tincture, etc., contain active principles which have not yet been thoroughly examined. Some of these principles have been isolated, and a few have been obtained in the crystalline condition; but their constitution has not been sufficiently well made out to admit of the classification of the bodies either among alkaloids, glucosides, acids, or other well-marked principles.

Andrographis Caules et Radix P.I., from *Andrographis paniculata*, Kariyat.

Anthemidis flores.

Apocynum. Canadian hemp.

Asclepias Tuberosa. Pleurisy root. (Asclepedin.)

Aurantii cortex. (Hesperidin.)

Azadirachtæ Cortex et Folia, P.I., from *Azadirachta Indica*, Nim or Margosa. (A resin; $C_{36}H_{50}O_{11}$. Broughton.)

Bonducellæ Semina, P.I., from *Cæsalpinia* (*Guilandina*) *Bonducella. Bonduc-seeds or nickar-nuts.*

Buchu folia.

Calendula officinalis. Marigold. (Calendulin, Stoltze.)

Calotropis Cortex, P.I., from *Calotropis procera* and *C. gigantea.* Mudar.

Canellæ cortex. (Cascarillin, $C_{12}H_{11}O_4$.)

Caulophyllum Thalictroides. Blue cohosh. Alkaloid?

Cimicifuga (*Actæa*) *racemosa* (Cimicifugin; said by Conard to be neutral, and by Falck alkaloidal). Black snake-root. (*Cimicifugæ Rhizoma*, B.P.)

Cypripedium pubescens (Cypripedin?). Ladies' Slipper.

Euonymus atropurpureus. Wahoo-bark. (Euonymin?)

Euonymi Cortex, B.P., is "the dried root bark," the source of *Extractum Euonymi Siccum*, B.P.

Eupatorium perfoliatum. Thoroughwort or Boneset.

Gulancha (*Tinosporæ Radix et Caules*, P.I.)

Gynocardiæ semina, from Gynocardia odorata. (*Chaulmugra*, P.I.)

Hamamelis Virginica. Witch-hazel.

The official portions are *Hamamelidis Cortex*, B.P., the source of *Tinctura Hamamelidis*, B.P., and *Hamamelidis Folia*, B.P., the source of *Extractum Hamamelidis Liquidum*, B.P.

Hydrocotyles Folia, P.I., from *Hydrocotyle Asiatica.* Indian pennywort.

Iris versicolor. Blue flag. (Iridin or Irisin?)

Lactuca. (Lactucin, etc.) The milk-juice, dried, yields *Lactucarium*, U.S.P.

Lappa, U.S.P., *Arctium Lappa*, *Lappa officinalis.* Burdock.

Lupulus.

Magnolia. Swamp sassafras, or beaver tree.

Marrubium. Horehound. Marrubein, a crystalline bitter substance (Mein).

Maticæ Folia. Matico.

Melia Azedarach. (Resin, Jacobs.)

Pepo. The seed of *Cucurbita Pepo.* A remedy for tapeworm.

Phytolacca Bacca et Radix. Pokeberry and root. Phytolaccin, a crystalline substance (Claassen).

Scutellaria. Skullcap.

Serpentaria. Virginia Snakeroot.

Soymidæ Cortex, P.I. Rohun Bark, from *Soymida febrifuga.*

Taraxaci Radix. (Taraxacin.)

Toddaliæ Radix, P.I.

Triticum repens. Rhizome of couch-grass.

Veronica Virginica, roots and rhizome. Culvers root; *Leptandra*, U.S.P. (Leptandrin ?).

Viburnum. Black haw. (*Viburnin.*)

ALKALOIDS.

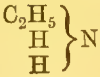
Constitution of Alkaloids, or Organic Bases.

Natural Alkaloids.—The natural organic bases, alkaloids, or alkali-like bodies (εἶδος, *eidos*, likeness), have many analogies with ammonia. Their constitution as a class is not yet satisfactorily known; but some are possibly direct derivatives of a single molecule of ammonia (NH_3), or of double, triple, or quadruple molecules (N_2H_6, N_3H_9, N_4H_{12}); others of ammonias in which the ammoniacal structure is largely merged in or conditioned by a benzenoid or aromatic structure; or *vice versâ*, in which the benzenoid character is conditioned by the ammoniacal; while others again certainly appear to be benzenoid but of a more or less nitrogen-benzene (pyridinoid) rather than a completely carbon-benzene character—benzene in which CH''' is displaced by N''' (p. 613).

Numerous artificial organic bases, having a simple ammoniacal constitution, have already been formed. These are sometimes termed *amido,—imido,—*and *nitrile—bases*, or *amines*, and are primary, secondary, and tertiary according as one, two, or three atoms of hydrogen in ammonia have been displaced by radicals, as seen in the following general formulæ (R = any univalent radical):—

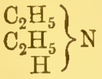
$$\left.\begin{matrix}R\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}R\\R\\R\end{matrix}\right\}N;$$

or in the following examples :—



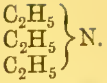
$\left.\begin{array}{r}C_2H_5\\H\\H\end{array}\right\}N$

Ethylamine, or ethylia (C_2H_7N).



$\left.\begin{array}{r}C_2H_5\\C_2H_5\\H\end{array}\right\}N$

Diethylamine, or diethylia ($C_4H_{11}N$).



$\left.\begin{array}{r}C_2H_5\\C_2H_5\\C_2H_5\end{array}\right\}N.$

Triethylamine, or triethylia ($C_6H_{15}N$).

The three classes have also been termed amidogen-bases (NH_2), imidogen-bases (NH), and nitrile-bases (N).

Formation of some of the Artificial Organic Bases.—A few illustrations will suffice. Just as the addition of iodide of hydrogen (HI) to ammonia (that is, the common, trihydrogen ammonia, NH_3), gives iodide of common ammonium (NHHHHI or NH_4I), so the addition of iodide of ethyl (C_2H_5I or EtI) (*see* page 480) to *ammonia* (NH_3) gives the iodide of ethyl-ammonium (NHHHEtI, or NH_3EtI, or $NH_3C_2H_5I$). A fixed alkali turns out common *ammonia* (NHHH) from the iodide (or any other salt) of common ammonium; it turns out ethyl-ammonia (NHHEt) from the iodide (or any other salt) of ethyl-ammonium. Ethyl-ammonia (or *ethylia*, or ethylamine), NHHEt, with iodide of ethyl, EtI, gives iodide of diethyl-ammonium [NHHEtEtI, or NH_2Et_2I, or $NH_2(C_2H_5)_2I$]. From the latter, potash turns out diethyl-ammonia ($NHEt_2$). Diethyl-ammonia (*diethylia*, or diethylamine) with iodide of ethyl, gives iodide of triethyl-ammonium ($NHEt_3I$). The latter with alkali gives triethyl-ammonia, or *triethylia*, or triethylamine (NEt_3), and this with iodide of ethyl gives iodide of tetrethyl-ammonium, NEt_4I, or $N(C_2H_5)_4I$.

What has just been stated respecting iodide of ethyl is true of other salts of ethyl; and what is true of salts of ethyl is true of salts of an immense number of other radicals—univalent, bivalent, etc.; so that a vast number of artificial organic bases and their salts can be produced. The reactions are not always so sharp as those just given. Mixtures of primary, secondary, and tertiary compounds, rather than either alone, often result in an experiment; but the reactions are typically true. Some of these artificial bases not only resemble natural alkaloids, but are strong caustic liquids, like solution of ammonia.

Then, the displacing radical in an artificial alkaloid or its salt may not only be of one kind, as indicated in the preceding paragraphs, but of different kinds; and while the radical displacing one atom of hydrogen is keeping its place, any of the many known radicals may occupy the position of one or all of the other atoms of hydrogen. Thus, for example, we have methyl-ethyl-amylamine ($C_8H_{19}N$, or $NCH_3C_2H_5C_5H_{11}$, or NMeEtAy), a colourless, oily body, of agreeable aromatic odour. The empirical formulæ of the vegeto-alkaloids morphine, quinine, etc., may some day be similarly resolvable into rational formulæ, either simply ammoniacal, benzenoid or pyridinoid. Their artificial production will then quickly follow. In a few cases this has already been accomplished.

Analogues of Amines.—From the analogy of phosphorus, arsenium and antimony to nitrogen, there exist, as might be expected, *phosphines*, *arsines*, and *stibines* ; bases resembling *amines*, but containing the respective elements (P,As,Sb) in place of the nitrogen (N) of the amines.

Methylamine (CH_3HHN) and *trimethylamine* $(CH_3)_3N$, are artificial ammoniacal alkaloids. The former was found by Schmidt, in *Mercurialis annua* and *M. perennis*, and previously by Reichardt, who termed it *mercurialine*. Trimethylamine is also produced in large quantities in the dry distillation of the evaporated residue of the spent wash produced in beetroot spirit distilleries.

Propylamine, or *tritylia* (C_3H_7HHN), is a volatile oil, one product of the destructive distillation of bones and other animal matters.

The organic bases derived from one molecule of ammonia are termed *monamines* ; from two molecules, *diamines* ; from three, *triamines* ; and from four, *tetramines* :—

$$\left.\begin{matrix}R\\R\\R\end{matrix}\right\}N \qquad \left.\begin{matrix}R_2\\R_2\\R_2\end{matrix}\right\}N_2 \qquad \left.\begin{matrix}R_3\\R_3\\R_3\end{matrix}\right\}N_3 \qquad \left.\begin{matrix}R_4\\R_4\\R_4\end{matrix}\right\}N_4$$

In these amines, any bivalent, trivalent, or quadrivalent radical may occupy the place of two, three, or four univalent radicals (R). The diethylene-diamine is used medicinally under the name *piperazine* ; its constitution is that of piperidine (*vide* Index), in which NH displaces CH_2.

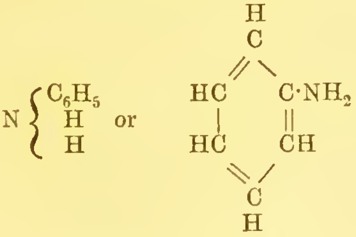
Wurtz first obtained methylamine and ethylamine in 1849; Hofmann, in 1850 and subsequently, added enormously to our knowledge of the secondary, tertiary, and other amines, and of the directly ammoniacal type of bodies generally. Kekulé linked on the aromatic or benzene type in 1865. Dewar and Körner almost simultaneously, in 1870, demonstrated the benzenoid character of pyridine and quinoline (see next paragraph), while no one has since been more active in alkaloidal research than Ladenburg.

Vegetal Alkaloids.—These are of great importance to the medical and pharmaceutical student. They are treated in considerable detail in the succeeding pages.

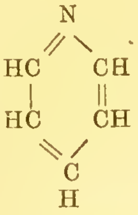
Animal Alkaloids.—Many well-known alkaloids occur in the juice of the flesh, and in other parts of animals. Ordinary extract of meat contains abundance of crystals of *creatine*, $C_4H_9N_3O_2$, and some *creatinine*, $C_4H_7N_3O$. Creatine easily parts with the elements of water and yields creatinine; it takes up the elements of water and yields *sarkosine*, $C_3H_7NO_2$, and *urea*, CH_4N_2O. Sarkosine is methyl-glycocoll. *Taurine*, $C_2H_7NSO_3$, may be obtained from bile; and it can be constructed artificially from its elements. Some animal tissues, as of the spleen, brain, and pancreas, yield, as a product of work, *leucine*, $C_6H_{13}NO_2$, which occurs in white, pearly crystals; also *tyrosine*, $C_9H_{11}NO_3$. Gautier recently obtained several new alkaloids from albumenoids, and hence termed them *leucomaines* (λεύκωμα, *leucoma*, white of egg), namely, *xanthocreatinine*, $C_5H_{10}N_4O$, *crusocreatinine*, $C_5H_8N_4O$, *amphicreatinine*, $C_9H_{19}N_7O_4$, and *pseudoxanthine*, $C_4H_5N_5O$. The leucomaines and the animal alkaloids generally are of great physiological interest. Some of the leucomaines are toxic and indistinguishable from ptomaines; in fact, the three classes merge into one another.

Ptomaines.—A series of diamines, many of them toxic, have been isolated, by Brieger, from decaying nitrogenous animal principles, including the putrid albumenoids or proteids of the human body itself—hence the name *ptomaines* (πτῶμα, *ptoma*, a corpse). These have some medico-legal importance, but, inasmuch as they may occur in life, poisoning the blood during the progress of disease, especially disease associated with the development of micro-organisms or microbes, that is, zymotic disease (ζύμη, *zumē*, ferment), they have great pathological interest—indeed, physiological interest also, for one of a curaroid character seems to play a part in the process of digestion. The names of some of these bases are *neurine* ($C_5H_{13}NO$) and *neuridine* ($C_5H_{14}N_2$), from putrid flesh; *muscarine* ($C_5H_{13}NO_2$) and *gadinine* ($C_7H_{16}NO_2$), from putrid fish; *cadaverine* ($C_5H_{16}N_2$), *saprine*, and *putrescine* ($C_4H_{12}N_2$), from putrid human remains, *choline* being met with in the earlier stages of decay; and *tetanine*, ($C_{13}H_{30}N_2O_4$), the administration of which to animals produced symptoms resembling those of tetanus in man, from beef putrified by the agency of the microbe which is associated with the cause of traumatic tetanus, so distressing to the human subject. *Tyrotoxicon* was the name given by Vaughan to a toxic ptomaine he isolated from poisonous cheese (τυρὸς, *turos*, cheese; τοξικόν, *toxicon*, poison), afterwards from poisonous milk and cream, which, taken as food, had caused more or less vomiting, headache, and diarrhœa. He afterwards recognised it as *diazobenzene* hydrate, $C_6H_5\cdot N:N\cdot OH$. Brieger states that when shell-fish is poisonous it is due to the presence of a ptomaine he has named *mytiloxine*, $C_6H_{15}NO_2$. Para- and meta-phenylene-diamine appear to have all the characters of leucomaines or ptomaines, the latter causing intense influenza.

Evidence of Constitution of the Natural Alkaloids.—Attempts to form artificially the more important natural organic bases commonly used in medicine have hitherto failed. Many artificial colorific alkaloids of the amidobenzene (aniline or phenylamine) type, and of a curious double nitrogen type (azo- or, rather, diazo-type; see the non-colorific diazobenzene, as above), have been obtained. But the type of the natural medicinal alkaloids seems rather to be found in *pyridine*, C_5H_5N. Pyridine is producible in various ways, but is contained in *bone-oil* (from the distillation of bones—whence, also, *pyrrol*, C_4H_5N, and thence *iodopyrrol*, or *iodol*, C_4I_4HN, a rival of iodoform), together with the homologues *picoline*, C_6H_7N (or methyl-pyridine, ortho-, meta-, or para-); *lutidine*, C_7H_9N; and *collidine*, $C_8H_{11}N$; forming an homologous series of *pyridine bases*, $C_nH_{2n-5}N$.

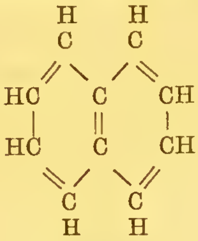


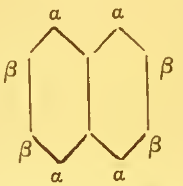
Phenylamine or amido-benzene.

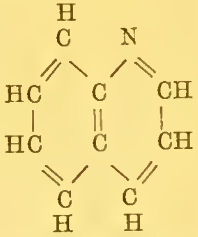


Pyridine.

From quinine, cinchonine, and strychnine, by the disruptive action of caustic alkalies, not only pyridine and homologues, but *quinoline* or *chinoline*, C_9H_7N, have been obtained; hence pyridine and quinoline would seem to contribute to the construction of those and similar alkaloids. Quinoline can be made in various other ways, especially (Skraup) from nitrobenzene, aniline and glycerine. Quinoline is closely related both to benzene and to pyridine (see the following formula). Its relation to naphthalene (two carbon-conjoined benzene residues) is the relation of pyridine to benzene.


Naphthalene.


Alpha and beta positions.


Quinoline.

Both pyridine and quinoline form additive compounds with hydrogen (*see* Piperidine in Index).

By adding six atoms of hydrogen to pyridine, piperidine is obtained, and conine, the alkaloid of hemlock, is piperidine with propyl (C_3H_7) replacing one of the hydrogen atoms. It has been formed artificially by Ladenburg from picoline (*see* also ecgonine, tropine, etc.).

Chemists, in the hope, doubtless, of discovering how to produce the valuable medicinal alkaloids artificially, have obtained several alkaloidal derivatives of quinoline. One, *kairine*, somewhat resembles quinine.

Again, alkaloids yield organic acids, and organic acids—notably those occurring in the nicotine-yielding and morphine-yielding plants—may be converted into pyridine compounds when the constituents of their molecules are interwoven with those of ammonia.

A careful consideration of the above and allied facts irresistibly leads to the inference that we are at last almost "within measurable distance" of the artificial production of most of the natural alkaloids. This is a subject of financial and general commercial weight; of considerable technological, including pharmaceutical, importance; of very great medical consequence, especially taken in connection with its ramifications; and of transcendent interest as illustrating the working of the forces of Nature within the molecules of matter.

Vegeto-animal alkaloids.—*Choline*, $C_5H_{15}NO_2$, occurs in the bile and the brain, also in ergot and ipecacuanha, hops, areca nut, cotton-seed cake, Scopola Japonica, etc. *Guanine*, $C_5H_5N_5O$, and *Sarkine*, $C_5H_4N_4O$, are found in flesh and in young plane leaves. Fresh meat furnishes *Carnine*, $C_7H_8N_4O_3$; and *Betaine*, $C_5H_{11}NO_2$, is found in beetroot, cotton-seed cake, and in urine.

Hydroxylamine.—Besides the amide, imide, and nitrile bases already mentioned, ammonia may have one atom of its hydrogen displaced by hydroxyl, hydroxylamine (NH_2OH) resulting. It is often formed when nascent hydrogen acts on an oxide of nitrogen, as when zinc, diluted sulphuric acid, and a little nitric acid are brought together. It yields substitution products, as ethylhydroxylamine (NHC_2H_5OH), and additive compounds, as hydrochlorate of hydroxylamine (NH_2OH,HCl):—

$$\underset{\text{Ammonia.}}{N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.} \qquad \underset{\text{Hydroxylamine.}}{N\left\{\begin{matrix}H\\H\\OH\end{matrix}\right.} \qquad \underset{\text{Ethylhydroxylamine.}}{N\left\{\begin{matrix}C_2H_5\\H\\OH\end{matrix}\right.} \qquad \underset{\text{Hydrochlorate of hydroxylamine.}}{N\left\{\begin{matrix}H\\H\\OH\end{matrix}\right. HCl}$$

Hydroxylamine and aldehydes yield *aldoximes*. Hydroxylamine and acetones yield *acetoximes*. (*Vide* Manuals, not limited to the requirements of medical and pharmaceutical students.)

Hydrazine, $H_2N—NH_2$. Diethylamine, by action of nitrous acid, yields a nitroso derivative which, on reduction, furnishes what apparently is a diamidic compound—diethylhydrazine $(C_2H_5)_2N—NH_2$. Hydrous hydrazine has the formula $H_2N—NH_2,H_2O$. Hydrazine itself cannot very easily be isolated. Its salts with ordinary acids are generally crystalline, and isomorphous with corresponding ammonium salts. Acidified, they have very powerful reducing properties, and act as strong poisons towards the lower organisms.

Azoimide or *imidazoic acid*, HN_3, is a body closely resembling the haloid acids, and was originally prepared by Curtius from hydrazine and ethyl hippurate; it may, however, be prepared more easily by a method proposed by Wislicenus, in which sodamide $NaNH_2$, prepared by passing NH_3 over melted sodium, is heated with nitrous oxide.

Note on Nomenclature of Natural Alkaloids.—The first syllables of the names of the natural alkaloids recall the name of the plant whence they were obtained, or some characteristic property. It is to be regretted that the last syllable is not either *ine* or *ia*, instead of sometimes one and sometimes the other. The termination in *ia* distinguishes the alkaloids from some other substances the names of which end in *ine*, as chlorine, bromine, iodine, fluorine, glycerine, gelatine, etc., but traders generally, and the compilers of the American, British, French, and German Pharmacopœias adopt the termination in *ine*. The names of the salts of the alkaloids are given on the assumption that the acid unites with the alkaloid without decomposition. Thus hydrochlorate (sometimes termed "hydrochloride") of morphine is regarded as morphine with added hydrochloric acid; as we might assume sal-ammoniac to be ammonia (NH_3) with hydrochloric acid (HCl), and name it hydrochlorate of ammonia (NH_3HCl), instead of chloride of ammonium (NH_4Cl). All acids, even sulphydric, unite with alkaloids and form additive salts having similar names.

Antidotes.—In cases of poisoning by alkaloids, emetics and the stomach-pump must be relied on rather than chemical agents. But astringent liquids may be administered, for tannic acid precipitates many of the alkaloids from their aqueous solution, absorption of the poison being thus possibly retarded.

MORPHINE AND OTHER OPIUM ALKALOIDS.

Formula of Morphine; $C_{17}H_{19}NO_3,H_2O$. Molecular weight, 303.

Occurrence.—Morphine, or morphia, occurs in opium (the inspissated juice of the fruit, termed the capsule, of the White Poppy, *Papaver somniferum*) as meconate of morphine [$(C_{17}H_{19}NO_3)_2$, $C_7H_4O_7$, $5H_2O$; Dott], and as sulphate. The dried poppy-capsule of pharmacy (*Papaveris Capsulæ*, B.P.) contains opium principles, but varying much in nature and proportion: tho presence of morphine, narcotine, and meconic acid have been demonstrated; and, by Groves, of codeine and narceine. Ordinary Asia-Minor opium (Turkey, Smyrna, or Constantinople opium) contains, when dried, from 10 to 15 per cent. of morphino. The British Pharmacopœia directs that opium used for officially recognised purposes, other than the manufacture of alkaloids, or of extract of opium of official strength, must contain not less than 9·5, and not more than 10·5 per cent. of morphine, when the opium is quantitatively analysed (*vide* Index) by the official method or by any trustworthy method of that date (1885).

Process for Hydrochlorate.—The hydrochlorate, $C_{17}H_{19}NO_3$, HCl, $3H_2O$ (*Morphinæ Hydrochloras*, B.P.), occurs in slender white acicular crystals; it is prepared by simply decomposing an aqueous infusion of opium with chloride of calcium, meconate of calcium and hydrochlorate of morphine being produced. (If the infusion, which is always acid, be first nearly neutralized by the cautious addition of small quantities of a very dilute solution of ammonia, the chloride of calcium then at once causes a precipitate of meconate of calcium, which can be filtered off, leaving a coloured solution of hydrochlorate of morphine. On the large scale—*vide* B.P.—the details are somewhat different.) The salt is partially purified by crystallization from the evaporated liquid, then by treatment of the solution of the impure hydrochlorate by animal charcoal, and lastly by precipitation of the morphine from the still coloured liquid by ammonia and re-solution of the morphine in hot dilute hydrochloric acid; hydrochlorate of morphine separates out on cooling.

Hydrochlorate of morphine deposited from a hot solution in about twenty times its weight of alcohol is anhydrous.

Morphine may also, of course, be prepared by the methods given for the assay of opium. (*See* Index.)

Process for Acetate.—Acetate of morphine ($C_{17}H_{19}NO_3$, $C_2H_4O_2$, $3H_2O$ (*Morphinæ Acetas*, B.P.), a white pulverulent salt, is prepared by dissolving morphine in acetic acid, the morphine being obtained from a solution of the hydrochlorate by precipitation with ammonia, or direct from opium. Fifteen parts of hydrochlorate yield, theoretically, sixteen of acetate. One grain of acetate in ten minims of water forms the *Injectio Morphinæ Hypodermica*, B.P.

Both the hydrochlorate and acetate of morphine are soluble in water, but the solution is not stable unless acidulated and containing alcohol; hence the official solutions, 1 per cent. (*Liquor Morphinæ Hydrochloratis*, B.P., and *Liquor Morphinæ Acetatis*, B.P.), consist of three parts water and one part rectified spirit, a few minims per ounce of hydrochloric or acetic acid being added. Even solid acetate of morphine is unstable, slowly dissociating into acetic acid and morphine; hence the acid odour of acetate of morphine; hence, too, the necessity, when a solution of acetate of morphine of perfectly definite strength is required, of preparing it from a weighed quantity of hydrochlorate, or of pure crystalline morphine. Other preparations official in the British Pharmacopœia are *Suppositoria Morphinæ*, *Trochisci Morphinæ*, *Trochisci Morphinæ et Ipecacuanhæ*, and *Liquor Morphinæ Bimeconatis*. The latter is made by dissolving morphine in a diluted spirituous solution of meconic acid. It contains about 1¼ per cent. of the so-called bimeconate of morphine ($C_{17}H_{19}NO_3C_7H_4O_7$?), and, so far, resembles tincture of opium.

Process for Sulphate.—Sulphate of morphine $(C_{17}H_{19}NO_3)_2H_2SO_4,5H_2O$ (*Morphinæ Sulphas*, B.P.) is prepared by neutralizing precipitated morphine with diluted sulphuric acid. It occurs in white silky crystals, not very soluble in water. A one per cent. solution in weak spirit forms the *Liquor Morphinæ Sulphatis*, B.P.

Solubility of morphine salts in water at 60° F.—According to Dott, 1 part of the respective salts is soluble in the annexed numbers of parts of water:—acetate, 2½; tartrate, 9¾; sulphate, 23; hydrochlorate, 24; meconate, 34.

Tartrate of Morphine has the formula $(C_{17}H_{19}NO_3)_2, C_4H_6O_6, 3H_2O$.

CODEINE, or *Codeia* ($C_{18}H_{21}NO_3, H_2O$), is another officially recognised alkaloid of opium (*Codeina*, B.P.). It is soluble in the slight excess of ammonia employed in the foregoing process for the separation of morphine. It is obtained by evaporating the ammoniacal liquors, "treating the residue with water, precipitating with caustic potash, and purifying the precipitated alkaloid by recrystallization from ether. It occurs in colourless or nearly colourless octahedral crystals; soluble in eighty parts of water and of solution of ammonia, readily soluble in spirit and in diluted acids. The aqueous solution has a bitter taste and an alkaline reaction. The alkaloid dissolves in sulphuric acid, forming a colourless solution, which, when gently warmed with molybdate of ammonium or a trace of perchloride of iron, assumes a deep-blue colour. Moistened with strong nitric acid, it becomes yellow but not red. Ignited in air, it yields no ash." It reduces a solution of one part of selenite of ammonium in twenty of strong sulphuric acid, yielding a green colour (Lafon). See also page 621.

Other alkaloids exist in opium. In the above process for morphine a considerable quantity of an alkaloid of very weak basic properties, *narcotine*, ($C_{22}H_{23}NO_7$), or $C_{19}H_{14}(CH_3)_3NO_7$ (*Narcotina*, P.I.), remains in the exhausted opium, and may be extracted by digesting in acetic acid, filtering, and precipitating by ammonia. It crystallizes in brilliant needles from alcohol or ether. The formula of its hydrochlorate is $C_{22}H_{23}NO_7,HCl,H_2O$. By oxidation it yields *cotarnine* and an acid termed *opianic*. From the mother-liquors there have also been obtained *thebaine* ($C_{19}H_{21}NO_3$), *papaverine* ($C_{21}H_{21}NO_4$, Hesse; $C_{20}H_{21}NO_4$, Merck), *opianine* ($C_{21}H_{21}NO_7$?), *narceine* ($C_{23}H_{29}NO_9$), *cryptopine* ($C_{21}H_{23}NO_5$), *meconin* ($C_{10}H_{10}O_4$), *meconoisin* ($C_8H_{10}O_2$), *laudanine* ($C_{20}H_{25}NO_4$), *codamine* ($C_{20}H_{25}NO_4$), *gnoscopine* ($C_{34}H_{36}N_2O_{11}$), *pseudomorphine* ($C_{17}H_{18}NO_3$), *protopine* ($C_{20}H_{19}NO_5$), *laudanosine* ($C_{21}H_{27}NO_4$), *hydrocotarnine* ($C_{20}H_{19}NO_5$), *rhœadine* ($C_{23}H_{21}NO_6$), *meconidine* ($C_{21}H_{23}NO_4$), *lanthopine* ($C_{23}H_{25}NO_4$). A little acetic acid also exists in all opium (D. Brown).

Analytical Reactions.

First Analytical Reaction.—To a minute fragment of a salt of morphine add one drop of water, and warm the mixture until the salt dissolves, then stir the liquid with a glass rod moistened by a strong *neutral* solution of perchloride of iron; a dirty-blue colour is produced.

Even in dilute solutions morphine reduces ferricyanide of potassium to ferrocyanide, hence may be detected by the blue precipitate (Prussian blue) produced on the addition of ferric chloride and ferricyanide. Other substances, but no other official alkaloids, give this reaction.

Second Analytical Reaction.—To a drop or two of a strong solution of a morphine salt in a test-tube add a minute fragment of iodic acid (HIO_3, page 346); iodine is set free. Into the upper part of the tube insert a glass rod covered with mucilage of starch, and warm the solution; dark-blue "starch iodide" is produced. If the mixture of morphine and iodic acid be shaken up with chloroform or bisulphide of carbon, a violet solution is obtained. This reaction is only confirmatory of others, as albuminous matters also reduce iodic acid.

Third Analytical Reaction.—To a few drops of an aqueous infusion of opium add a drop of *neutral* solution of ferric chloride; a red solution of the meconate of iron is produced. Add solution of corrosive sublimate; the colour is not destroyed (as it is in the case of sulphocyanate of iron, a salt of similar tint). In cases of poisoning by a preparation of opium, this test is almost as conclusive as a direct reaction of morphine (the poison itself), meconic acid being obtainable from opium only.

Other Reactions.—Add carbonate of sodium to a solution of a salt of morphine; a white precipitate of morphine falls, slowly and of a crystalline character if the solution is dilute. Collect this precipitate and moisten it with neutral solution of perchloride of iron; the bluish tint above referred to is produced.——Add an alkali to a solution of hydrochlorate or acetate of the alkaloid; morphine is precipitated, soluble in excess of the fixed alkali, far less readily so in ammonia.——Moisten a particle of a morphine salt with nitric acid; an orange-red coloration is produced. Warm a little morphine with strong sulphuric acid and arseniate of sodium, blue-green tinges result.——To morphine add strong sulphuric acid, mix, and strew nitrate of bismuth on the fluid; the mixture turns dark brown or black.——Heat morphine on platinum foil; it burns entirely away.

APOMORPHINE ($C_{17}H_{17}NO_2$).

Apomorphine (ἀπὸ, *apo*, from, and *morphine*) is an alkaloid obtained from morphine by Matthiossen and Wright. It possesses remarkable physiological effects; one-tenth of a grain (in aqueous solution) injected under the skin, or a quarter of a grain taken into the stomach, produces vomiting in from four to ten minutes.

Process.—Hydrochlorate of morphine is hermetically sealed in a thick tube with considerable oxcess of hydrochloric acid, and heated to nearly 300° F. for two or three hours. The product is purified by diluting the contents of the tube with water, precipitating with bicarbonate of sodium, and treating the precipitate with ether or chloroform.——On shaking up the ethereal or chloroform solution with a very small quantity of strong hydrochloric acid, the sides of the vessel become covered with crystals of the hydrochlorate of the new base (*Apomorphinæ Hydrochloras*, B.P.). These may be drained from the mother-liquor, washed with a little cold water, in which the salt is sparingly soluble, recrystallized from hot water, and dried on bibulous paper or over sulphuric acid. The formula ($C_{17}H_{17}NO_2HCl$) indicates that the new alkaloid is derived from morphine by abstraction of the elements of water. "From solutions, bicarbonate of sodium throws down a precipitate which becomes green on standing and then forms a purple solution with ether, violet with chloroform, and bluish green with alcohol. With dilute solution of perchloride of iron it gives a deep red and with nitric acid a blood-red coloration." Two grains of the hydrochlorate dissolved in 100 minims of camphor-water constitute the *Injectio Apomorphinæ Hypodermica*, B.P.

Codeine, also, according to the same chemists, yields apomorphine by similar treatment, a reaction that would seem to indicate that codeine is methyl-morphine; indeed, Grimaux (Hesse also) has since obtained codeine—or, possibly, an isomer of codeine, methyl-morphine—from morphine. Codeine may also be obtained by heating a sodium compound of morphine, $C_{17}H_{18}NaNO_3$, with iodide of methyl, CH_3I; iodide of sodium and methyl-morphine or codeine result.

Codeine neither gives a blue colour with ferric chloride nor a red with nitric acid. Both codeine and morphine when heated with a mixture of strong sulphuric acid and arseniate of sodium give a blue colour, the morphine yielding a greenish blue and the codeine a violet blue.

Constitution of the opium alkaloids.—The opium alkaloids, like the cinchona alkaloids, have been attacked by many highly skilled chemists in the hope that analytical or, in a sense, destructive investigation would lead to synthetical or constructive knowledge; and many interesting and promising results have been obtained. But the subject is not yet sufficiently advanced for presentation before the younger students of medicine or pharmacy.

QUESTIONS AND EXERCISES.

Write some general formulæ of artificial alkaloids.—Name the substances represented by the following formulæ :—

$$\left.\begin{matrix}C_3H_7\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}C_3H_7\\C_3H_7\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\C_2H_5\\C_5H_{11}\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right\}N,\quad \left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N$$

What is the assumed constitution of the salts of the alkaloids ?—Describe the treatment in cases of poisoning by alkaloids.—Give the official process for the preparation of hydrochlorate of morphine. In what form does morphine occur in opium ?—How is acetate of morphine prepared ?—What plan is adopted for preventing the decomposition of the official solutions of morphine ?—Mention the analytical reactions of morphine.—In addition to the reactions of morphine, what test may be employed in searching for opium in a liquid or semi-fluid material ?—How is apomorphine prepared ? and what are its properties ?—Describe the relation of morphine to codeine.

QUININE AND OTHER CINCHONA ALKALOIDS.

Formula of Quinine ; $C_{20}H_{24}N_2O_2,3H_2O$. Molecular weight, 378.

Source.—Quinine and other alkaloids exist in the varieties of cinchona bark as *kinates*, or rather, *quinates*.* In the British Pharmacopœia cinchona bark is defined as "the dried bark of Cinchona Calisaya, *Weddell ;* Cinchona officinalis, *Linn. ;* Cinchona succirubra, *Pavon ;* Cinchona lancifolia, *Mutis ;* and other species of Cinchona from which the peculiar alkaloids of the bark may be obtained." The official galenical preparations are made with the Succirubra or Red Cinchona Bark (*Cinchonæ Rubræ Cortex*, B.P.). Quinine, quinidine, and cinchonine also occur, together with cupreine, in the bark of various species of Remijia, known as Cuprea bark.

Extraction of the Mixed Alkaloids.—Mix about two ounces of powdered bark with a quarter of its weight of lime and a little water, and extract with benzoated amylic alcohol. (For a description of this operation, see "Quinine, quantitative estimation of," in the Index.) Shake the product in a separating funnel, with an ounce of water acidulated with sulphuric or hydrochloric acid. Draw off the aqueous liquid, which will contain the alkaloids as acid salts, and add to it a slight excess of ammonia. Collect the precipitated alkaloids on a filter, wash, and dry in the air or over a dish of sulphuric acid covered by a bell-glass. For the separation of alkaloids, *see* Index, "De Vrij's process"; an operation which should not be attempted at this stage of study.

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* *Quinic acid*, $C_7H_{12}O_6$, occurs in cinchona, coffee, holly, ivy, oak, elm, etc. Heated it yields *hydroquinone*, $C_6H_4(OH)_2$. Oxidized it gives quinone, $C_6H_4O_2$, which is probably a di-ketone, $C_4H_4(CO)_2$, dicarbonyl benzene, or $C_2H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_2H_2$ The homologues of benzene yield other "quinones."

Process for Sulphate of Quinine.—Sulphate of quinine (*Quininæ Sulphas*, B.P.) is prepared by treating the yellow bark with diluted hydrochloric acid, precipitating the resulting solution of hydrochlorate of quinine by soda, and redissolving the precipitated quinine in the proper proportion of hot diluted sulphuric acid; or by extracting with spirit, etc., after the addition of lime (see the sections on the quantitative analysis of cinchona bark). This, the common commercial sulphate, crystallizes out on cooling in silky acicular crystals, one molecule containing two atoms of quinine ($2C_{20}H_{24}N_2O_2$), one of sulphuric acid (H_2SO_4), and eight of water of crystallization ($8H_2O$).

Sulphate of quinine, the *common* or so-called *disulphate* —$(C_{20}H_{24}N_2O_2)_2,H_2SO_4,8H_2O$,—is only slightly soluble in water; on the addition of diluted sulphuric acid the so-called *neutral sulphate* or *soluble sulphate* ($C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$), is formed, which is freely soluble. The latter salt may be obtained in large rectangular prisms.* An *acid sulphate* ($C_{20}H_{24}N_2O_2$, $2H_2SO_4$, $7H_2O$) also exists. The *Infusum Cinchonæ Acidum*, B.P., contains the soluble sulphate.

The ordinary disulphate of quinine is more soluble in alcohol or alcoholic liquids than in water. An Ammoniated Tincture (*Tinctura Quininæ Ammoniata*, B.P.) is made by dissolving the sulphate in proof spirit and adding a large excess of solution of ammonia. This tincture contains quinine itself liberated from combination by, and dissolved by aid of the excess of, the ammonia. Quinine wine (*Vinum Quininæ*, B.P.) is a solution of neutral sulphate and citrate of quinine in orange wine, made by dissolving the disulphate (one grain in the ounce) in orange wine by the help of citric acid. The remaining pharmacopœial preparations of quinine are the hydrochlorate and the mixed citrates of iron, ammonium, and quinine (*Ferri et Quininæ Citras*, B.P.), the well-known scale compound. The latter is made by dissolving ferric hydrate, prepared from ferric sulphate, and quinine, prepared from the sulphate, in solution of citric acid, ammonia also being added: the liquid, evaporated to a syrupy consistence and dried in thin layers on glass plates, yields the usual greenish-yellow scales (*vide* p. 174).

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* We do not know whether or not these sulphates are ordinary sulphates, the hydrogen of the acid going over to the quinine molecule, nor whether or not the quinine molecule is univalent or bivalent; hence we cannot say whether the *common* sulphate or the *soluble* sulphate is, in constitution, the neutral sulphate. In the above paragraph, the names *disulphate*, *neutral sulphate*, *acid sulphate*, indicate nothing more than that the first sulphate contains in one molecule two atoms (chemical atoms) of quinine to one of sulphuric acid, the second one of each, and the third two of acid to one of quinine.

Hydrochlorate of Quinine (*Quininæ Hydrochloras*, B.P.) is prepared by neutralizing quinine by hydrochloric acid. Its formula is $C_{20}H_{24}N_2O_2,HCl,2H_2O$. It is soluble in about 34 parts of water at common temperatures, the sulphate requiring 700 or 800. The two salts resemble each other in appearance, but the crystals of the hydrochlorate are commonly somewhat larger than those of the sulphate. 8 grains of hydrochlorate of quinine dissolved in 1 ounce of tincture of orange-peel forms the *Tinctura Quininæ*, B.P.

Basic Citrate of Quinine has the formula $(C_{20}H_{24}N_2O_2)_2 \cdot H_3C_6H_5O_7, 5H_2O$. Other citrates contain three molecules of quinine to two of citric acid, and one of quinine to one of citric acid.

REACTIONS.

First Analytical Reaction.—To a solution of quinine or its salts in acidulated water add fresh chlorine-water, shake, and then add solution of ammonia; a green coloration (*thalleioquin*, or dalleiochin) is produced. Bromine-water or bromine-vapour may be used instead of chlorine.

Second Analytical Reaction.—Repeat the foregoing reaction, but precede the addition of solution of ammonia by that of solution of ferrocyanide of potassium; an evanescent red coloration is produced (Livonius and Vogel).

Third Analytical Reaction.—To an aqueous solution of a soluble salt of quinine add solution of oxalate of ammonium; a white crystalline precipitate of oxalate of quinine falls. It is soluble in acids. If the solution to be tested be made from ordinary sulphate of quinine, excess of the latter should be added to water very faintly acidulated with sulphuric acid, and the undissolved crystals removed by filtration.

Fourth Analytical Reaction.—A saturated aqueous solution of any neutral salt of quinine is made by dissolving so much of the salt in hot water as that some shall separate when the mixture has cooled to about 60° F. After standing for some time, filter. To the filtrate water-washed ether is added until a distinct layer of ether remains undissolved, and then ammonia in slight excess. After agitation and rest for fifteen minutes, all precipitated quinine will have re-dissolved.

Note.—In the case of quinidine salts well-defined crystals appear at the junction of the aqueous and ethereal layers, especially after standing. In the case of cinchonidine salts a thick layer of small crystals appears at once. In the case of cinchonine salts the undissolved alkaloid makes the ethereal layer nearly solid. In testing quinine for other alkaloids evaporate the aqueous solution to one-fifth.

Fifth Analytical Reaction.—Formation of Iodo-sulphate of Quinine. Dissolve sulphate of quinine in weak spirit of wine slightly acidulated with sulphuric acid, and add an alcoholic solution of iodine; a black precipitate forms. Allow the precipitate to settle, pour away the fluid, wash once or twice with cold alcohol and then boil with alcohol; on cooling minute crystals separate, having the optical properties of the mineral tourmaline. This iodo-sulphate is sometimes termed Herapathite, from the name of one of the chemists who discovered it (in 1852). Under the name of iodide of hydriodate of quinine, Bouchardat described and used it in 1845. It is so slightly soluble in alcohol that by its means quinine can be fairly well separated from its admixture with the other cinchona alkaloids. According to Jörgensen it has the formula $4C_{20}H_{24}N_2O_2$, $3H_2SO_4$, $2HI$, I_4,xH_2O.

Sixth Analytical Reaction.—Prepare a saturated solution of ordinary sulphate of quinine in water at about 60° F., and add to 5 volumes of that solution 7 volumes of solution of ammonia (sp. gr. 0·96). The alkaloid which at first precipitates redissolves upon slight agitation if the sulphate of quinine is free from anything but traces of other cinchona alkaloids. If, however, more than traces of quinidine, cinchonidine, and cinchonine salts be present, a permanent precipitate remains. This is Kerner's method of testing sulphate of quinine for other cinchona alkaloids. It turns upon the fact that the solubility of the sulphates of the cinchona alkaloids in water is in the opposite order to the solubility of the alkaloids themselves in solution of ammonia.

Other Characters.—Concentrated sulphuric acid dissolves quinine with production of only a faint yellow colour, which is not increased by warmth.——Quinine and its salts, heated on platinum foil, burn entirely away.——Most salts of quinine when in solution have a beautiful blue fluorescence. They twist the ray of polarized light to the left.——Quinine is soluble in alcohol, ether, benzol, and chloroform. Ordinary quinine sulphate is insoluble in chloroform, and but slightly soluble in water. Its solubility in chloroform is increased by the presence in solution of quinidine and cinchonine sulphates (Prescott), and its solubility in water is decreased by the presence in solution of ammonium sulphate (Carles). The slight solubility of its sulphate and iodo-sulphate in water distinguishes quinine from the other cinchona alkaloids, including the "amorphous alkaloid," or "quinoidine."

Quinidine ($C_{20}H_{24}N_2O_2$, the *conquinine* or *conchinine* of Hesse) is an isomer of quinine. Its salts are fluorescent, and give thalleioquin with chlorine- or bromine-water and ammonia. They twist the ray of polarized light to the right. Quinidine is insoluble in water and sparingly soluble in ether (*see* Quinine, 4th Analytical Reaction). It is soluble in alcohol, benzol, and chloroform. It is less soluble than quinine in ammonia, 5 volumes of a saturated aqueous solution of its ordinary sulphate requiring 60 to 80 volumes of ammonia solution (sp. gr. 0·96). Its sulphate is more soluble in water and chloroform than the sulphate of quinine. Tartrate of quinidine is soluble in water. The hydriodate is insoluble in water and weak spirit, and occurs as sandy crystals. The hydriodates of the other cinchona alkaloids, though more soluble than quinidine hydriodate, are sometimes precipitated from neutral concentrated solutions, as amorphous or semi-liquid precipitates. These, however, are soluble in weak spirit.

Cinchonidine ($C_{20}H_{24}N_2O$).—The sulphate (*Cinchonidinæ Sulphas*, B.P.) is official. It may be obtained from the mother-liquids of the crystallization of sulphate of quinine. When perfectly pure, salts of cinchonidine do not give thalleioquin and are not fluorescent. Even good commercial salts, however, nearly always give both reactions. Salts of cinchonidine twist the polarized ray to the left. Cinchonidine is insoluble in water and nearly so in ether. (*See* Quinine, 4th Analytical Reaction). It is soluble in alcohol, benzol, and chloroform. It is less soluble in ammonia solution than quinine, 5 volumes of a saturated aqueous solution of cinchonidine sulphate requiring about 80 volumes of ammonia solution (sp. gr. 0·96). It is true cinchonidine is dissolved as readily as quinine if excess of strong ammonia is quickly mixed with the solution of the salt of cinchonidine; but from such a solution cinchonidine soon crystallizes out, while quinine remains dissolved for many hours. Sulphate and hydriodate of cinchonidine are soluble in water, but the sulphate, like quinine sulphate, is insoluble in chloroform. Tartrate of cinchonidine is insoluble in water; and in this form cinchonidine is usually separated from neutral solutions containing the other cinchona alkaloids except quinine, the filtrate from the precipitate of tartrate yielding cinchonine on the addition of ammonia.

Cinchonine ($C_{20}H_{24}N_2O$) is an isomer of cinchonidine. The sulphate (*Cinchoninæ Sulphas*, B.P.) is official. "It may be obtained from the mother-liquors of the crystallization of the sulphates of quinine, cinchonidine, and quinidine, by precipitating the alkaloid with caustic soda, washing it with spirit until free from other alkaloids, dissolving in sulphuric acid, and, after purifying the solution with animal charcoal, allowing to crystallize.". When quite pure, its salts are not fluorescent and do not give thalleioquin. As in the case of cinchonidine, even good commercial specimens of cinchonine salts nearly always give both reactions. Cinchonine salts twist the polarized ray to the right. Cinchonine is insoluble in water and nearly so in ether. (*See* Quinine, 4th Analytical Reaction.) It is soluble in chloroform, benzol, and alcohol. Chloroform containing one-fourth of its weight of 95 per cent. alcohol dissolves cinchonine much more readily than either alcohol or chloroform alone. Cinchonine is insoluble in ammonia solution. Sulphate, tartrate, and hydriodate of cinchonine are soluble in water, and the sulphate, like sulphate of quinidine, is soluble in chloroform. In mixtures of cinchona alkaloids this alkaloid is precipitated by alkali after the others have been successively removed by ether, tartrate of sodium, and iodide of potassium.

Constitution of the cinchona alkaloids.—This is not yet clear, though great advances have been made. In the course of the investigations derivatives of quinoline, more or less resembling quinine have been obtained, namely, *kairine*, *kairoline* and *thalline; antipyrin* also. (*Acetanilide*, or "antifebrin," has, too, been found to possess greater antipyretic powers than the derivatives just mentioned.) *See* also p. 613.

"*Quinoidine*, "*chinoidine*," or the "*amorphous alkaloid*." —Cinchona barks generally contain some alkaloid isomeric with quinine which, like quinine, is soluble in ether, but the ordinary sulphate and iodosulphate of which are not crystalline and are soluble. These salts are semi-solid resinous-looking substances. The iodo-sulphate is used in De Vrij's method for the separation of mixed alkaloids. Quinoidine is usually obtained along with quinine, etc., from the mixed alkaloids by ether, and remains in the mother liquor, from which it is precipitated by an alkali.

Cinchovatine occurs in a particular variety of cinchona bark. *Quinicine*, and *cinchonicine*, are alkaloids produced by the action of heat on quinine or quinidine and on cinchonidine respectively. They, also, are isomers, Hesse says polymers, of the parent alkaloids. Both yield ordinary salts. *Quiniretin* is the name given to the brown or reddish-brown indifferent substance into which quinine in aqueous solution is converted when exposed to much light.

Quinamine ($C_{20}H_{26}N_2O_2$), is a fifth cinchona alkaloid obtained by Hesse in 1872 from the bark of *Cinchona succirubra*. Its solution is not fluorescent, and does not give thalleioquin. The same chemist announces the presence in cinchona of a sixth alkaloid, *cinchamidine* ($C_{20}H_{26}N_2O$).

Cupreine, ($C_{19}H_{22}N_2O_2$) is an alkaloid discovered, simultaneously, by Howard and Hodgkin, by Paul and Cownley, and by Whiffen, in the bark of a Remijia (allied to Cinchona) and termed *cuprea* bark. It closely resembles quinine, but is sparingly soluble in ether. It may be converted into quinine by heating its sodium compound with methyl chloride; whence it appears that quinine is the methyl ether of cupreine. The alkaloid at first termed *homoquinine* or *ultraquinine* seems to have been a mixture of cupreine and quinine.

Hydroquinine, $C_{20}H_{26}N_2O_2$, containing two more atoms of hydrogen than are present in the quinine molecule, is an alkaloid associated with quinine, in minute amount, in cinchona bark. It remains in the mother-liquor when quinine sulphate is crystallized from an acid solution. Its therapeutic action is similar to that of quinine. Its characters are closely allied to those of quinine. It was discovered by Hesse.

STRYCHNINE.

Formula, $C_{21}H_{22}N_2O_2$. Molecular weight, 334.

Source.—Strychnine or strychnia exists, to the extent of about 1 per cent., in Nux Vomica (*Strychnos Nux-vomica*), also (Shenstone) in minute quantity in the bark of the Nux Vomica tree (false angostura bark) and to 1·0 or 1·5 per cent. in St. Ignatius's bean (*Strychnos Ignatius*), chiefly in combination with strychnic or igasuric acid, or, after slight fermentation when moistened, with lactic acid. Crow also found it in the bark of the *S. Ignatius*.

Process.—According to the official process for its preparation (*Strychnina*, B.P.), the seeds, disintegrated by subjection to steam, and, after drying, grinding in a coffee-mill, are exhausted with spirit, the latter removed by distillation, the extract dissolved in water, colouring and acid matters precipitated by acetate of lead, the filtered liquid evaporated to a small bulk, the strychnine precipitated by ammonia, the precipitate washed, dried, and exhausted with spirit, the spirit recovered by distillation, and the residual liquid set aside to crystallize. Crystals of strychnine having formed, the mother-liquor (which contains the brucine of the seeds) is poured away, and the crystals of strychnine washed with spirit (to remove any brucine) and recrystallized.

Properties.—Strychnine occurs "in right square octahedrons or prisms, colourless and inodorous; sparingly soluble in water, but communicating to it an intensely bitter taste; soluble in boiling rectified spirit and in chloroform, but not in absolute alcohol or in ether." It forms salts with acids. The *sulphate* has the formula, $(C_{21}H_{22}N_2O_2)_2H_2SO_4$, $6H_2O$. It is soluble in about 40 parts of water. The *citrate* $(C_{21}H_{22}N_2O_2)_2C_6H_8O_7$, $4H_2O$ (or $6H_2O$) dissolves, at 60° F., in about 40 parts of water and 115 parts of alcohol. The hydrochlorate seems to have the formula $C_{21}H_{22}N_2O_2HCl,3H_2O$, and (Dott) is soluble in $35\frac{1}{2}$ parts of water.

REACTIONS.

First Analytical Reaction.—Place quite a small fragment of strychnine on a white plate, and near to it also a small piece of red chromate of potassium; to each add one drop of concentrated sulphuric acid; after waiting a minute or so for the chromate to fairly tinge the acid, draw the latter, by a glass rod, over the strychnine spot; a beautiful purple colour is produced, quickly fading into a yellowish red. The following oxidizing agents may be used in the place of the chromate:—puce-coloured oxide of lead, fragments of black oxide of manganese, ferricyanide of potassium, or permanganate of potassium.

This reaction is highly characteristic; a minute fragment dissolved in much dilute alcohol, or, better, chloroform, and one drop of the liquor evaporated to dryness on a porcelain crucible-lid or other white surface, yields a residue which immediately gives the purple colour on being oxidized in the manner directed.

Other Reactions.—Strong sulphuric acid does not act on strychnine, even at the temperature of boiling water, a fact of which advantage is taken in separating strychnine from other organic matter for the purposes of toxicological analysis.——Sulphocyanate of potassium produces, even in dilute solutions of strychnine, a white precipitate, which, under the microscope, is seen to consist of tufts of acicular crystals.

——Strong nitric acid does not colour strychnine in the cold, and on heating only turns it yellow.

The Physiological Test.—A small frog placed in an ounce of water to which $\frac{1}{100}$ of a grain of salt (acetate) of strychnine is added, is, in two or three hours, seized with tetanic spasms on the slightest touch, and dies shortly afterwards.

Strychnine has an intensely bitter taste. Cold water dissolves only $\frac{1}{2000}$ part; yet this solution, even when largely diluted, is distinctly bitter. Alcohol is a somewhat better solvent. The salts of the alkaloid are more soluble. The official solution (*Liquor Strychninæ Hydrochloratis*, B.P.) contains 1 per cent. of strychnine, the solvent being three-parts water, one part spirit, and a few minims (6 per ounce) of hydrochloric acid (rather more than sufficient to form hydrochlorate of strychnine). If too much acid be present, the hydrochlorate will crystallize out in cold weather.

BRUCINE, or BRUCIA ($C_{23}H_{26}N_2O_4$, $4H_2O$), is an alkaloid accompanying strychnine in Nux Vomica and St. Ignatius's bean to the extent of about two per cent. It is readily distinguished by the intense red colour produced when nitric acid is added to it. *Igasurine*, once supposed to be a third alkaloid of nux vomica, has been shown by Shenstone to be only a mixture of brucine and strychnine.

Curarine ($C_{10}H_{15}N$), the active principle of the arrow-poison, termed *curari*, *urari*, *ourari*, *wourali*, or *woorara*, prepared from a *Strychnos*, resembles strychnine in giving colour by oxidation, but the colour is more stable. Iodide or platinocyanide of potassium do not with curarine afford precipitates which crystallize from alcohol like those of strychnine. Curarine, also, is soluble in water. Unlike strychnine, curarine is reddened by sulphuric acid; it, also, is not dissolved out by ether from an acid or alkaline liquid. *Curari* appears to vary much in strength and quality. It is probably a mixture of vegetable extracts.

Distinction of Brucine from Morphine.—The red coloration produced by the action of nitric acid on brucine is distinguished from that yielded with morphine by the action of reducing agents (such as stannous chloride, hyposulphite of sodium, sulphydrate of sodium), which decolorize the morphine-red, but change that of the brucine to violet and green (Cotton). The solution of brucine in the nitric acid should be heated to the boiling-point, diluted with water, and the stannous chloride then be added.

Distinction of Free Alkaloids or their Salts from each other.—This is accomplished by remembering the appearance and other physical characters of the substances as met with in pharmacy, the effect of heat, the action of such solvents as water, alcohol, and ether, the influence of strong and diluted acids, strong and weak alkalies, oxidizing substances, and other reagents. Tables to aid in the analysis of small quantities of official alkaloids, their salts, glucosides, and various "scale" compounds, will be found opposite page 649.

QUESTIONS AND EXERCISES.

What alkaloids are more or less characteristic of the different varieties of cinchona bark? In what form do they occur?—By what method is sulphate of quinine obtained?—Give the characters of sulphate of quinine.—Describe the tests for quinine.—How would you detect salicin in sulphate of quinine?—Show how the sulphates of quinidine or cinchonine may be proved to be present in commercial sulphate of quinine.—How are cinchonine and quinine distinguished from morphine?—Whence is strychnine obtained?—Describe the official process for the isolation of strychnine.—Give the characters of strychnine.—Describe the tests for strychnine.—By what reagent is brucine distinguished from strychnine?—Distinguish between brucine and morphine.—By what general methods would you distinguish common alkaloids from each other?

ALKALOIDS OF LESS FREQUENT OCCURRENCE.

Aconitine, Aconitina, or Aconitia, is an alkaloid obtained from Aconite (*Aconitum Napellus*) leaves (*Aconiti Folia*, B.P.) and root (*Aconiti Radix*, B.P.). The alkaloid itself is only slightly soluble in water; it occurs in the plant in combination with a vegetable acid, forming a soluble salt.

Process.—The official process for its preparation (*Aconitina*, B.P.), consists in dissolving out the natural salt of the alkaloid from the root by rectified spirit, recovering the latter by distillation, mixing the residue with water, filtering, precipitating the aconitine by ammonia, drying the precipitate and digesting it in ether (in which some of the accompanying impurities are insoluble), recovering the ether by distillation, dissolving the dry residue in the retort in water acidulated by sulphuric acid, again precipitating the alkaloid by ammonia, and finally washing and drying.

Properties.—Aconitine usually occurs as a white powder. It has been obtained and studied in the crystalline state by Groves, Wright, Williams and others. It is very slightly soluble in cold water, more so in hot, and much more soluble in alcohol, in ether, and in chloroform. It is one of the most violent poisons known. "When rubbed on the skin, it causes a tingling sensation, followed by prolonged numbness." The thousandth part of a grain on the tip of the tongue produces, after a minute or so, a characteristic tingling sensation and numbness; large quantities rubbed into the skin cause numbness and loss of feeling. Sulphuric acid turns it of a yellowish and, afterwards, dirty violet colour.

According to Wright, who, in conjunction with Groves and Williams, worked by the aid of grants from the British Pharmaceutical Conference, *Aconitum Napellus* yields, chiefly, crystalline *aconitine*, $C_{33}H_{43}NO_{12}$, with some crystalline *pseud-aconitine*, $C_{36}H_{49}NO_{12}$, and a little non-crystalline alkaloid.

In the research laboratories of the Pharmaceutical Society of Great Britain, Dunstan and Umney found, in addition to aconitine ($C_{33}H_{45}NO_{12}$ Dunstan and Ince), aconine, and an amorphous alkaloid, *napelline* or *isaconitine*, whose salts are also uncrystallizable. It is isomeric with aconitine and also yields the same products on hydrolysis. Aconitine is readily hydrolyzed into *aconine*, $C_{26}H_{41}NO_{11}$, and benzoic acid (Dunstan and Passmore).

According to Jürgens the formula of aconitine is $C_{33}H_{47}NO_{12}$. On allowing an acetic solution containing iodide of potassium to evaporate to dryness, and then adding water, crystals of hydriodate of aconitine of characteristic appearance remain.

The tuberous roots of *Aconitum Ferox* and other species constitute the *bish* or *bikh* of India (*Aconiti Ferocis Radix*, P.I.). It chiefly contains the variety of aconitine termed *pseudaconitine*. Some of the aconitine of pharmacy is pseudaconitine.

According to Paul and Kingzett, the alkaloid of Japanese aconite has the formula $C_{29}H_{43}NO_{9}$, while Wright and Menke state that the formula is $C_{66}H_{88}N_{2}O_{21}$, and name it *japaconitine.*

Unguentum Aconitinæ, B.P., contains eight grains of the alkaloid to one ounce of benzoated lard.

Aconitum heterophyllum, *Atis*, or *Atees*, or *Wakhma* (*Acon-*

iti Heterophylli Radix, P.I.), contains no aconitine, but an alkaloid *ateesine* having the formula $C_{46}H_{74}N_2O_5$.

ASPIDOSPERMINE, $C_{22}H_{30}N_2O_2$, is an alkaloid of *Quebracho blanco* bark (Fraude). Another and different alkaloid is *quebrachine* ($C_{21}H_{26}N_2O_3$) (Hesse). The latter chemist has isolated four other closely related alkaloids; and two from *Quebracho colorado* bark.

ATROPINE, or ATROPIA ($C_{17}H_{23}NO_3$).—This alkaloid has hitherto been considered to exist ready formed in the Belladonna, or Deadly Nightshade (*Atropa Belladonna; Belladonnæ Folia et Radix*, B.P.), as soluble acid malate of atropine. But the observations of Messrs. Schering and the researches of Will indicate that not atropine but an isomer of atropine, namely hyoscyamine, is the alkaloid chiefly and often solely present, and that the alkaline treatment, during the process of extraction, converts the hyoscyamine into atropine. Hyoscyamine solutions rotate a plane-polarized ray to the left; atropine has no optical rotatory power. Each similarly affects the eye.

Process.—Atropine is obtained by exhausting the root with spirit, precipitating the acid and some colouring-matter by lime, filtering, adding sulphuric acid to form sulphate of atropine (which is somewhat less liable to decomposition during subsequent operations than the alkaloid itself), recovering most of the spirit by distillation, adding water to the residue, and evaporating till the remaining spirit is removed; solution of carbonate of potassium is then poured in till the liquid is nearly, but not quite neutral, by which resinous matter is precipitated: the latter is filtered away, excess of carbonate of potassium then added, and the liberated atropine dissolved out by shaking the liquid with chloroform. The latter solution, having subsided, is removed, the chloroform recovered by distillation, the residual atropine dissolved in warm spirit, colouring-matter separated by digesting the liquid with animal charcoal, the solution filtered, evaporated, and set aside to deposit crystals.

Solubility.—Atropine is sparingly soluble in water, the liquid giving an alkaline reaction—more soluble in alcohol and ether.

Tests.—Atropine solutions give with perchloride of gold a yellow precipitate. One drop of a dilute aqueous solution (two grains to the ounce) powerfully dilates the pupil of the eye. It is generally applied on a piece of thin tissue-paper or small disc (*Lamellæ Atropinæ*, B.P.) placed between the eyelid and the eye. *Hydrobromate of homatropine* is official (*Homatropinæ Hydrobromas*, B.P.). It is a white crystalline powder or aggregation of minute prismatic crystals, soluble in six parts of cold water, and in one hundred and thirty-three of ethylic alcohol. The dilute aqueous solution powerfully dilates the pupil of the eye. A two per cent. aqueous solution is not precipitated by the cautious addition of solution of ammonia previously diluted with twice its volume of water [distinction from atropine]. About a tenth of a grain moistened with two minims of nitric acid and evaporated to dryness on the water-bath yields a residue which is coloured yellow by an alcoholic solution of potash [distinction from atropine, hyoscine, and hyoscyamine]. If about a tenth of a grain be dissolved in a little water and the solution be made alkaline with ammonia and shaken with chloroform, the separated chloroform will leave on evaporation a residue which will turn yellow, and finally brick-red when warmed with about fifteen minims of a solution of two grains of perchloride of mercury in a hundred minims of proof spirit. For Gerrard, Schweissinger, and Flückiger have observed that *homatropine* (Ladenburg's oxytoluyltropeine, a physiologically similar but less powerful and therefore sometimes more useful alkaloid than atropine), like hyoscyamine and atropine, has unusually powerful alkaline properties, precipitating mercuric oxide from mercuric solutions, reddening phenolphthaleïn, and, with warmth, blackening calomel. No other ordinary alkaloids are so powerfully alkaline.

Baryta water decomposes atropine into *tropine* ($C_8H_{15}NO$), and *tropic acid* ($C_9H_{10}O_3$), a molecule of water being absorbed ; hence the atropine, so called, would seem to be *tropate of tropine*, minus water, or *tropyl-tropine*. Indeed Ladenburg, by heating tropic acid and tropine in sealed tubes, has produced a base indistinguishable from atropine. The same chemist by removing the elements of water from tropine gets *tropidine*, $C_8H_{13}N$, closely related to ecgonine (p. 639) and anhydro-ecgonine. This is, possibly, an intermediate member of a group of alkaloids, of which others are *conine*, $C_8H_{15}N$, and *collidine*, $C_8H_{11}N$, the latter a product of the destructive distillation of bone-oil, coal, quinine, etc. Commercial atropine is said by Regnauld and Valmont to be a mixture of true atropine with hyoscyamine.

In the so-called Japanese belladonna (*Scopola Japonica*) occurs *scopoleine*, an alkaloid resembling, but more powerful than atropine (Eykman); but Schmidt considers that only atropine, hyoscyamine and hyoscine are present.

Preparations.—The alkaloid itself (*Atropina*), its sulphate (*Atropinæ Sulphas*), a colourless powder soluble in water, (made by neutralizing atropine with sulphuric acid), a solution (*Liquor Atropinæ Sulphatis*, 1 per cent.), and an ointment (*Unguentum Atropinæ*, eight grains per ounce), are the preparations official in the British Pharmacopœia.

The fluorescence of alkaline solutions of extract of belladonna is caused by *chrysatropic acid*, $C_{12}H_{10}O_5$ (Kunz), probably allied to the fluorescent *scopoletin*, $C_{10}H_8O_4$, found in Japanese belladonna by Eykman.

BAPTITOXINE.—Schrœder gives this name to a poisonous alkaloid in *Baptisia tinctoria*, wild indigo, in which he also finds the glucosides *baptisin* and *baptin*.

BEBERINE, BEBIRINE, or BIBIRINE, ($C_{36}H_{42}N_2O_6$), is an alkaloid in the bark of Bebeeru, or Bibiru (*Nectandra Rodiœi*).

Process.—According to the British Pharmacopœia, it, or rather its sulphate, $C_{36}H_{42}N_2O_6$, H_2SO_4 (*Beberinæ Sulphas*, B.P.), may be prepared by exhausting the bark (*Nectandræ Cortex*, B.P.) with water acidulated by sulphuric acid, concentrating, removing most of the acid by lime, filtering, precipitating the alkaloid by ammonia, filtering, drying, dissolving in spirit (in which some accompanying matters are insoluble), recovering most of the spirit by distillation, neutralizing by diluted sulphuric acid, evaporating to dryness, dissolving the residual sulphate in water, evaporating to the consistence of a syrup, and spreading on glass plates, drying the product at 140° F. Thus obtained, it occurs in dark-brown translucent scales, yellow when powdered, strongly bitter, soluble in water and in alcohol. It is probably a mixture of sulphates of beberine, nectandrine, and other alkaloids.

Tests.—Alkalies give a pale-yellow precipitate of beberine when added to an aqueous solution of a salt of the alkaloid; the precipitate is soluble in ether. With red chromate of potassium and sulphuric acid, beberine gives a black resin, and with nitric acid a yellow resin.

Buxine, from the bark of *Buxus sempervirens*; *pelosine*, or *cissampeline*, from the root (*Pareiræ Radix*, B.P.) of *Cissampelos Pareira*; and *paricine*, from a false Para cinchona-bark, are probably identical with Beberine (Flückiger).

Nectandrine ($C_{40}H_{46}N_2O_8$, $4H_2O$).—Drs. Maclagan and Gamgee a few years ago discovered this second alkaloid in Bebeeru-bark. It differs from beberine in fusing when placed in boiling water, in being much less soluble in ether, in giving with strong sulphuric acid and black oxide of manganese a beautiful green and then violet coloration, and in having a distinct molecular weight. They considered that two other alkaloids exist in Bebeeru-bark.

BERBERINE ($C_{20}H_{17}NO_4$), is an alkaloid existing in several plants of the natural order *Berberideæ* (three species yield *Indian Barberry*, *Berberis Cortex*, P.I.), in Calumba-root (*Calumbæ Radix*, B.P.) in the root of *Coptis Teeta*, *or Mishmi Bitter* (*Coptidis Radix*, P.I.), an Indian tonic, and in many other yellow woods. *Hydrastis Canadensis*, or *Golden Seal*, contains berberine, though another alkaloid, *hydrastine* ($C_{22}H_{23}NO_6$), related to narcotine (which seems to be methoxyl-hydrastine; Schmidt) and to papaverine, and even a third, are said to be present, all, in Perkin's opinion, benzene derivatives of iso-quinoline. Tho dried rhizome and rootlets are official, *Hydrastis Rhizoma*, B.P., and these are the source of *Extractum Hydrastis Liquidum*, B.P., and *Tinctura Hydrastis*, B.P. The root of *Berberis vulgaris* contains berberine and (Wacker) *oxyacanthine* ($C_{18}H_{19}NO_3$; $C_{19}H_{21}NO_3$ Rüdel), as well as (Hesse) *berbamine* (also $C_{18}H_{19}NO_3$). *Xanthorrhiza apiifolia*, an old American tonic, and, apparently, *Xanthoxylon Fraxineum*, or Prickly Ash, also contain berberine. The rhizome of *Menispermum Canadense*, *Yellow Parilla*, contains, according to Maisch, a colourless alkaloid as well as berberine. The colour of the tissues of these vegetables is apparently due to berberine; for the alkaloid itself is remarkable for its beautiful yellow colour.

Tests.—When a dilute solution of iodine and iodide of potassium is added to a solution of any salt of berberine in hot spirit, excess of iodine being carefully avoided, brilliant green spangles are deposited. The reaction is sufficiently delicate to form, according to Perrins, an excellent test of the presence of berberine. This iodo-compound polarizes light, and has other analogies with herapathite.

Berberine itself is not official; but plants in which it occurs are used as medicinal agents in all parts of the world.

Process.—Berberine is readily extractod by boiling the raw material with water, ovaporating the strained liquid to a soft extract, digesting the residue in alcohol, recovering the alcohol by distillation, boiling the residue with diluted sulphuric acid, filtering and setting aside; the sulphate of berberine separates out, and may be purified by recrystallization from hot water. The neutral sulphate, $(C_{20}H_{17}NO_4)_2H_2SO_4$, is very soluble in water, the acid sulphate, $C_{20}H_{17}NO_4, H_2SO_4$, is less soluble. The alkaloid itself is obtained by shaking hydrate of lead with a hot aqueous solution of the sulphate of berberine (Procter).

CAFFEINE.—*See* THEINE.

CAPSICINE.—M. Felletár obtained from Capsicum-fruits (*Capsici Fructus*, B.P.), which when ground form *cayenne Pepper*, a volatile alkaloid having the smell of conine. Thresh has obtained crystalline hydrochlorate and sulphate. The latter chemist has also succeeded in isolating the active principle of capsicum, which he has termed *capsaicin* $(C_9H_{14}O_2)$, a crystalline non-alkaloidal excessively acrid substance. Its exact chemical character is not yet made out. According to Dr. Thresh a similar pungent principle occurs in ginger (gingerol) and in grains of paradise (paradol), bodies probably isomeric with capsaicin. (*See* also *Capsicin*, in Index).

CARPAINE, $C_{14}H_{27}NO_2$, occurs in *Carica papaya.*

COCAINE $(C_{17}H_{21}NO_4)$, is an alkaloid of *Erythroxylon Coca* (*Coca*, B.P.), the leaves of which act powerfully as a restorative to the human system. The hydrochlorate of the alkaloid is official (*Cocainæ Hydrochloras*, B.P.); also a ten per cent. solution of the same (*Liquor Cocainæ Hydrochloratis*, B.P.), preserved by aid of salicylic acid. Cocaine and its salts may be prepared by agitating with petroleum spirit a strong, acidulated, aqueous extract of the leaves made alkaline with carbonate of sodium, well shaking the separated spirit with acidulated water, treating the separated acid fluid with ether and excess of carbonate of sodium, washing out the alkaloid from the ether by water acidulated with hydrochloric acid, and finally evaporating the resulting aqueous solution of the hydrochlorate to the crystallizing point. Cocaine may be precipitated with ammonia and recrystallized from alcohol, ether, or warm benzene. From this pure cocaine the pure and very soluble hydrochlorate may be prepared by neutralizing with hydrochloric acid and crystallizing.

Prolonged contact of cocaine with hot water, acids, alkalies, or even alcohol, is undesirable, as cocaine readily breaks up into benzoyl-ecgonine, and methylic alcohol,

$C_{17}H_{21}NO_4 + H_2O = C_{16}H_{19}NO_4 + CH_3OH$, benzoyl-ecgonine afterwards yielding ecgonine and benzoyl-hydrate or benzoic acid, $C_{16}H_{19}NO_4 + H_2O = C_9H_{15}NO_3 + C_7H_6O_2$. In coca other bases occur with cocaine. Paul and Cownley, also Giesel, find *cinnamyl-cocaine.* Hesse finds *cocamine* and *cocaidine* isomeric with cocaine. Liebermann finds several bases, one of which is poisonous, namely, *isatropylcocaine*, $C_{19}H_{23}NO_4$, containing isatropyl in place of the benzoyl group in ordinary cocaine. It has an amorphous and sticky appearance. All these bases are easily hydrolysed, yielding ecgonine; the latter with benzoic anhydride yields benzoyl-ecgonine; and this with iodide of methyl, or otherwise, yields benzoyl-methyl ecgonine, or ordinary cocaine. By thus building up with other acidulous bodies than the benzoic a whole chemical series of "cocaines" can be produced.

Another alkaloid (benzoyl-pseudo tropeine) yielding instead of ecgonine a compound isomeric with tropine, also occurs in coca (Giesel, Liebermann).

Cocaine hydrochlorate occurs in colourless acicular crystals soluble in water, chloroform, alcohol, amylic alcohol; very slightly in ether; not readily decomposed even when boiled in water. The free alkaloid is readily decomposed by water, especially when the solution is warmed. The solution in water has a bitter taste; gives a purple precipitate with permanganates; and a white precipitate with ammonia. Its solution produces on the tongue a tingling sensation followed by numbness. The aqueous solution dilates the pupil of the eye. It gives no colour to cold strong acids, but chars with hot sulphuric acid. Evaporated to dryness on a water-bath with nitric acid, and treated with alcoholic potash, it develops an odour resembling peppermint. Besides its action as a restorative when taken internally, cocaine brought into contact with the mucous membrane of the eye, mouth, throat, etc., produces local anæsthesia. According to Squibb, good coca yields ·5 per cent. of cocaine. Cocaine may be detected in presence of other alkaloids by giving a yellow precipitate of the chromate with potassium chromate or chromic acid *in presence of free hydrochloric acid.*

COLCHICINE, the active principle of *Colchicum autumnale* (*Colchici Cormus*, B.P.; *Colchici Semina*, B.P.), is said to be an alkaloid, though some investigators think it has more of the characters of a neutral substance, and give it the name *colchicin.* Hertel gives it the formula $C_7H_{23}NO_6$, and states that ebullition with acidulated water converts it into *colchicein*, $C_{16}H_{21}NO_5 2H_2O$, and methyl alcohol. Zeisel says it may be crystallized from chloroform and offers the following formulæ for it and its derivative; *colchicin*, $C_{21}H_{22}(OCH_3)NO_5$; *colchicein*, $C_{21}H_{22}(OH)NO_5$. The most active medicinal preparation is an extract made from the *fresh* seeds by digestion in large volumes of alcohol of at least 90 per cent., and subsequent digestion of the marc in hot water. The extracts left on evaporating the two fluids separately are to be carefully mixed (Mols).

CONINE, CONIA, CONYLIA, CONICINE, or CICUTINE.—Formula, $C_8H_{17}N$ (Hofmann) or *α-normal-propyl-piperidine*, $C_5H_{10}N(C_3H_7)$. This alkaloid is a volatile liquid, occurring in Hemlock (*Conium maculatum*) in combination with an acid (malic?). It is not official. According to Petit its boiling point is 170° C., and its density 0·846. It forms crystalline salts.

Process.—It may be obtained by distilling hemlock-fruit (*Conii Fructus*, B.P.) with water rendered slightly alkaline by caustic soda or potash, or by similarly treating the fresh juice of the leaves. The alkaloid is a yellow oily liquid, floating on the water that distils over; by redistillation it is obtained colourless and transparent.

The salts of conine have no odour, but when moistened with solution of an alkali yield the alkaloid, the strong smell of which, at once recalling hemlock, is characteristic. Juice of hemlock-leaves (*Conii Folia*, B.P.), to which solution of potash and boiling water have been added, forms the official Inhalation of Conine (*Vapor Coninæ*, B.P.).

Tests.—Sulphuric acid turns conine purplish red, changing to olive-green; nitric acid a blood-red; perchloride of gold produces a yellowish-white precipitate, perchloride of platinum no precipitate, in aqueous solutions.

Hemlock also contains *methyl-conine*, $(C_8H_{16})''CH_3N$? (Kekulé and Von Planta), and *conhydrine*, $C_8H_{17}NO$.

The latter by dehydration yields a base, $C_8H_{15}N$. Kekulé's base is probably a methylic derivative of this, $C_8H_{14}CH_3N$, and not true methyl-conine.

According to Schiff, conine isomeric, at least, with the natural alkaloid, may be produced artificially by action of ammonia on butyric aldehyde and destructive distillation of the resulting compound. Ladenburg has produced conine identical with the natural alkaloid from α-picoline. Conine may now therefore be said to be a product of organic synthesis, producible from its elements.

Corydaline is an alkaloid obtained by Wenzoll from "Turkey Corn," the tubers of *Dicentra* (*Corydalis*) *formosa.*

Cusparine, ($C_{20}H_{19}NO_3$), with *cusparidine* ($C_{19}H_{17}NO_3$), and *galipine* ($C_{20}H_{21}NO_3$), are alkaloids occurring in the bark of *Galipea cusparia*, or true Angostura Bark (*Cuspariæ Cortex*, B.P.). The bitter principle, *angosturin*, is not an alkaloid.

Cytisine or Ulexine is an alkaloid found in laburnum and furze, and is also probably identical with *sophorine*, from *Sophora lomentosa.*

Daturine.—*Vide* Hyoscyamine.

Delphine, or Delphinine and Delphinoidine are the poisonous alkaloids of Stavesacre (*Delphinium Staphisagria*). The powdered seeds of the plant are employed to kill the *pediculi* of animals. The seeds (*Staphisagriæ Semina*, B.P.) contain about 25 per cent. of oil. *Unguentum Staphisagriæ*, B.P., contains about 10 per cent. of oil.

Ditamine (Jobst and Hesso), present in the *Ditain* of Gruppe, is an alkaloid of "Dita," or bark of *Echites scholaris*, or *Alstonia scholaris* (*Alstoniæ Cortex*, P.I.), a reputed febrifuge. Others are *echitamine* and *echitenine.* Oberlin and Schlagdenhauffen state that the allied *Alstonia constricta* (the bark of which is said to have advantages over the hop as a dietetic bitter), contains a crystalline alkaloid, *alstonine*, and uncrystallizable *alstonicine.* Alstonine seems to be allied to strychnine.

Duboisine.—*Vide* Hyoscyamine.

Emetine, ($C_{30}H_{44}N_2O_4$, Glenard; $C_{30}H_{40}N_2O_5$, Kunz).—This alkaloid is the active emetic principle of the root of *Cephaelis Ipecacuanha* (*Ipecacuanha*, B.P.). It occurs to the extent of 1 to 2 per cent. in the root, less in the stems, in combination with ipecacuanhic acid. The nitrate is peculiarly slightly soluble in water (Lofort). In the *Pulvis Ipecacuanhæ Compositus*, B.P., or "Dover's Powder" (Powdered Ipecacuanha, 1 part; Powdered Opium, 1 part; and Sulphate of Potassium, 8 parts), minute division of the active ingredients is promoted by prolonged trituration with sulphate of potassium, which is a very hard salt. In the pharmacopœia of the United States, sugar of milk is the diluent. *Ipecacuanha Wine* (*Vinum Ipecacuanhæ*, B.P.) is a solution of neutral acetate of emetine, and of other matters extracted (by aid of acetic acid) from the root, in sherry wine. *Acetum Ipecacuanhæ*, B.P., is obtained from 1 part of root in 20 of diluted acetic acid. Choline (Arndt', a "volatile base") has been found in ipecacuanha. Ipecacuanha is said to have pharmacological activity (in dysentery) even after all emetine has been extracted, hence it would seem to contain more than one active principle.

The Indian substitute of ipecacuanha is the dried leaf (*Tylophoræ Folia*, P.I.) of *Tylophora asthmatica.* Its active principle has not been satisfactorily isolated.

GELSEMINE, ($C_{11}H_{19}NO_2$, Sonnenschein; $C_{12}H_{14}NO_2$, Gerrard; $C_{54}H_{69}N_4O_{12}$, Thompson), is one of the alkaloids of *Gelsemium nitidum*, or Carolina Yellow Jasmine (*Gelsemium*, B.P.), in the tissues of which plant the *gelseminic acid* of Wormley, and *æsculin* ($C_{15}H_{16}O_9$), the fluorescent glucoside of the Horse Chestnut and of many other plants, are also present. Like strychnine, gelsemine is not apparently affected by strong sulphuric acid. Nitric acid does not colour it. A mixture of sulphuric acid and peroxide of manganese colours it a crimson red, changing to green. In *Gelsemium elegans* Crow finds an allied alkaloid which does not resist the action of strong sulphuric acid. *Gelseminine* is another alkaloid, said to be more powerful than gelsemine.

GRINDELINE is the name given by Fischer to a bitter crystalline alkaloid he extracted from *Grindelia* (*robusta*), U.S.P. The plant also contains a resin and a volatile oil.

GUARANINE.—*See* THEINE.

HYDRASTINE.—*See* p. 637.

HYOSCYAMINE, ($C_{17}H_{23}NO_3$), occurs in the leaves (*Hyoscyami Folia*, B.P.), and other parts of Henbane, Belladonna, Stramonium, and various species of Scopola; also (Dymond) in Lettuce. It forms brilliant colourless needles. Its salts also are crystalline. Its effect on the eye is similar to that of atropine. The researches of Ladenburg show that hyoscyamine is the tropate of an alkaloid isomeric with tropine. (*See* ATROPINE.) Ladenburg also finds in henbane some *hyoscine*, $C_{17}H_{21}NO_4$, identical with "scopolamine" from *Scopola atropoides* and *S. carniolica*, a tropate of another alkaloid isomeric (but not identical—Hesse, Schmidt) with tropine.

The alkaloids which occur in *Datura Stramonium*, or-

Thornapple (*Stramonii Semina et Folia*, B.P.), *Dhatura* (*Datura alba; Daturæ Folia et Semina*, P.I.), and in *Duboisia Myoporoides*, and were formerly supposed to be distinct alkaloids, called respectively *Daturine* and *Duboisine*, are identical with hyoscyamine, and the latter is isomeric with atropine (Ladenburg). Duboisine may however be identical with hyoscine. Indeed, according to Schmidt, the alkaloid of *Duboisia myoporoides* is sometimes hyoscyamine and sometimes hyoscyine or scopolamine. Bees which sip from the flowers of stramonium are said to produce poisonous honey.

Hyoscyamine melts when heated to between 108° and 109° C., and then is soon converted into atropine. Its solutions in alcohol or ether are stable, but the presence of a very minute amount of fixed caustic alkali, or a very little alkaline carbonate, causes complete conversion of the hyoscyamine into atropine. With chloride of gold its salts give a yellow crystalline precipitate.

JABORANDINE and JABORINE.—*See* PILOCARPINE.

JERVINE, ($C_{30}H_{46}N_2O_3$), occurs in *Veratrum album*, White Hellebore, and *V. viride*,* American White Hellebore, the root of which is officially recognised in Great Britain (*Veratri Viridis Rhizoma*, B.P.). Its salts are much less soluble in water than those of veratrine. According to Bullock, *Veratrum viride* contains still another alkaloid—*veratroidine*; and, according to Mitchell, *Veratrum album* also contains an alkaloid which he terms *veratralbine*. Tobien gives the formula of jervine as $C_{27}H_{47}N_2O_8$, and of veratroidine as $C_{51}H_{78}N_2O_{16}$, or $C_{24}H_{37}NO_7$. According to Wright, *Veratrum album* contains jervine, $C_{26}H_{37}NO_3$; pseudojervine, $C_{29}H_{43}NO_7$; rubijervine, $C_{26}H_{43}NO_3$; veratralbine, $C_{28}H_{43}NO_5$; and traces of veratrine, $C_{37}H_{63}NO_{11}$. The same author finds *Veratrum viride* to contain jervine, pseudojervine, cevadine, $C_{32}H_{42}NO_9$, rubijervine and traces of veratrine and veratralbine. Pehkschen finds jervine $C_{14}H_{22}NO_2$, pseudojervine, $C_{29}H_{49}NO_{12}$, and veratroidine $C_{32}H_{53}NO_9$, while Salzberger, besides jervine, rubijervine and pseudojervine, finds proto-veratrine $C_{32}H_{51}NO_{11}$ and protoveratradine $C_{26}H_{45}NO_8$. Salzberger confirms Wright and Luff's formula for jervine.

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* The name *Green Hellebore* is sometimes applied to this drug, but properly belongs to *Helleborus viridis* (*vide* "Helleborin" in Index), which is medicinal in some parts of Europe.—*Hanbury*.

Lobeline.—A volatile fluid alkaloid first isolated from the dried flowering herb *Lobelia inflata* (*Lobelia*, B.P.) by Procter. In the pure state it is inodorous, impure it smells slightly of the plant, but mixed with ammonia it emits a strong and characteristic smell of the herb. With acids it forms salts. A solid alkaloid is said to be present also.

Lupuline is stated by Greismayer to be a liquid volatile alkaloid contained in the Hop, *Humulus Lupulus* (*Lupulus*, B.P.).

Nectandrine.—*Vide* Beberine.

Nicotine, $C_{10}H_{14}N_2$, or $(C_5H_7)'''_2N_2$, or *hexahydrodipyridyl*, $C_{10}H_8(H_6)N_2$.—This also is a volatile liquid alkaloid, forming the powerful active principle of Tobacco (*Nicotiana Tabacum*), malate and citrate of nicotine being the forms in which it occurs in the leaf (*Tabaci Folia*, B.P.). Its odour is characteristic; like conine, it yields a precipitate with perchloride of gold; but, unlike that alkaloid, its aqueous solutions are precipitated yellowish white by perchloride of platinum. It is not official. It is also contained in *Pituri*, a drug "chewed by the natives of some parts of Australia as a stimulant narcotic," though, according to Liversedge, the latter alkaloid may have the formula $C_{12}H_{16}N_2$.

Physostigmine ($C_{15}H_{21}N_3O_2$).—An alkaloid obtained from the Calabar Bean (*Physostigmatis Semen*, B.P.), the seed of *Physostigma venenosum* (Jobst and Hesse) "by dissolving the alcoholic extract in water, filtering, adding bicarbonate of sodium, shaking the mixture with ether, and evaporating the ethereal liquid." It occurs "in colourless or pinkish crystals, slightly soluble in water, but readily soluble in alcohol and in diluted acids. The aqueous solution has an alkaline reaction, when warmed with or when shaken with dilute solution of potash becomes red, and when evaporated to dryness with ammonia over a water-bath leaves a bluish residue, the acidified solution of which is beautifully dichroic, being blue and red." A trace of it powerfully contracts the pupil of the eye (*Lamellæ Physostigminæ*, B.P.); a small quantity is highly poisonous. Fraser also isolated another (but, possibly, the same) principle, and termed it *Eserine*, from Esere, the name of this ordeal-poison at Calabar. Eber states that physostigmine, by action of acids, etc., takes up the elements of water and becomes *eseridine*, $C_{15}H_{23}N_3O_3$, an alkaloid one-sixth the strength of physostigmine, and occurring to some extent in the Calabar bean itself.

PILOCARPINE is, apparently, the active principle of the diaphoretic and sialogogue *Pilocarpus pennatifolius* (*Jaborandi*, B.P.). The occurrence of an alkaloid in this plant was first announced by Hardy, followed almost immediately by Byasson. A crystalline nitrate and hydrochlorate were first obtained by Gerrard. The leaves also yield an essential oil, a terpene $C_{10}H_{16}$ (Hardy). Harnack and Meyer state that the true formula for pilocarpine is $C_{11}H_{16}N_2O_2$, and that its effects resemble those of nicotine, but that jaborandi yields another alkaloid, *jaborine*, which probably closely approaches pilcarpine in composition, though allied to atropine in effects. One salt is official, the nitrate (*Pilocarpinæ Nitras*, B.P.), $C_{11}H_{16}N_2O_2$, HNO_3. This alkaloid is obtained from extract of jaborandi by shaking it with chloroform and a little alkali, and evaporating the chloroformic solution. The product, neutralized by nitric acid, and purified by recrystallization, yields the nitrate as a white granular powder or as prismatic crystals. It has a faintly bitter taste, and is soluble in water and in rectified spirit. Strong sulphuric acid forms with it a yellowish solution which, on the addition of red chromate of potassium, gradually acquires an emerald-green colour. It leaves no ash when burned with free access of air. It causes contraction of the pupil of the eye. Merck states that a third alkaloid, *pilocarpidine*, $C_{10}H_{14}N_2O_2$, is present in jaborandi. Harnack thinks that pilocarpine is probably a methyl derivative of pilocarpidine. The suggestion also is offered that the formula for nicotine differing only by O_2 from pilocarpidine, the latter is, perhaps, only dihydroxyl-nicotine. According to Merck, confirmed by Hardy and Calmels, jaborine is derived from pilocarpine by natural oxidation, while pilocarpidine similarly yields *jaboridine*, $C_{10}H_{12}N_2O_3$. The latter chemists have obtained pilocarpine artificially, "β-pyridine α-lactic acid" being converted into pilocarpidine, and this into pilocarpine.

PIPERINE, ($C_{17}H_{19}NO_3$), is a feeble alkaloid occurring in *White*, *Black* (*Piper Nigrum*, B.P.), *Long Pepper* (*Chavica officinarum*, Mign.), and *Cubeb Pepper* (*Cubeba*, B.P.), associated with volatile oil and resin; to these three substances the odour, flavour, and acridity belong. Piperine is obtained on boiling white pepper with alcohol, and evaporating the liquid with solution of potash, which retains resin. Recrystallized from alcohol, piperine forms colourless prisms fusible at 212° F. With acids and certain metallic compounds it forms salts, and distilled with strong alkali yields *piperidine* or *piperidia* ($C_5H_{10}HN$), an alkaloid of strong chemical properties, and *piperic acid* ($C_{12}H_{10}O_4$). Piperidine is interesting as being one of the alkaloids that has been obtained, artificially, by Ladenburg. It is hexa-hydro-pyridine, and is obtained by the action of nascent hydrogen on pyridine. Johnstone finds it in long pepper and in ordinary pepper, more especially in the husk. According to Buchheim the amorphous resin of the peppers is similar in constitution to piperine, alkalies breaking it up into piperidine and *chavicic acid. Pyrethrin* is also said to be a member of the series. The piperine of cubeb pepper is not to be confounded with *cubebin*, a neutral constituent and having the formula $C_{10}H_{10}O_3$; a derivative, probably, of pyrocatechin.

SANGUINARINE is the alkaloid of *Blood Root* (*Sanguinaria Canadensis*). Its salts are red. Konig and Tietz find five distinct alkaloids in the root of sanguinaria, viz. *chelerythrine*, $C_{21}H_{17}NO_4$; *sanguinarine*, $C_{20}H_{15}NO_4$; *a-homochelidonine*, $C_{21}H_{21}NO_5$; *β-homochelidonine*, $C_{21}H_{21}NO_5$; and *protopine*, $C_{20}H_{17}NO_5$. Protopine was found in opium by Hesse (who assigned it the formula $C_{20}H_{19}NO_5$). It also occurs in chelidonium; and probably is identical with *macleyine* obtained by Eyckmann from *Macleya cordata.*

SOLANINE, ($C_{43}H_{69}NO_{16}$).—An alkaloid existing in the Woody Nightshade, or Bitter-sweet (*Solanum dulcamara*). It occurs also in the shoots, and in minute amount in the skins of the tubers of the Potato (*Solanum tuberosum*). This alkaloid is only slightly soluble in water, alcohol, or ether; nitric acid colours it yellow; sulphuric acid produces at first a yellow, then a violet, and finally a brown coloration. It is said to be a conjugated compound of sugar with *solanidine* ($C_{25}H_{39}NO$). Geissler finds *dulcamarin* ($C_{22}H_{34}O_{10}$), a glucoside, to be the bitter constituent of *Solanum dulcamara.* A mixture of sulphuric acid and alcohol, or either selenic acid or selenate of sodium and sulphuric acid, colours solanine or solanidine a dark red.

SPARTEINE, ($C_{15}H_{26}N_2$), is a poisonous volatile alkaloid occurring in Broom-tops (*Scoparii Cacumina*, B.P.). Its discoverer, Stonhouse, considers that the diuretic principle of broom is *Scoparin*, a non-poisonous body, sparingly soluble in cold water. Mills has obtained ethyl-sparteine ($C_{15}H_{25}C_2H_5N_2$) and diethyl-sparteine ($C_{15}H_{24}C_2H_5C_2H_5N_2$). Apparently sparteine contains two pyridine nuclei.

STILLINGINE.—Bichy states that this alkaloid is present in *Stillingia sylvatica* or *Queen's Root.*

TAXINE, $C_{37}H_{52}O_{10}N$? is an alkaloid occurring in the yew.

THEINE, or CAFFEINE, or GUARANINE (Methyl-Theobromine) ($C_8H_{10}N_4O_2$, H_2O).—This alkaloid occurs in Tea, 2 to 4½ per cent.; Coffee, 1·2 per cent.; Maté or Paraguay Tea, ·2 to 2 per cent.; Guarana, 5 per cent.; and the Kola-nut. Infusions and preparations of these vegetable products are used, chiefly as beverages, by three-fourths of the human race. It is remarkable that the instinct of man, even in his savage state, should have led him to select, as the bases of common beverages, just the four or five plants which out of many thousands are the only ones, so far as we know, containing theine.

Theine is volatile. Considerable quantities may be collected by condensing the vapours evolved during the roasting of coffee on the large scale. The infusion of tea, from which astringent and colouring matters have been precipitated by solution of subacetate of lead, and which has been evaporated to a small bulk, yields a precipitate of theine on the addition of a strong solution of carbonate of potassium. It may be crystallized from alcohol or by sublimation. Theine forms salts with acids (*Caffeinæ Citras*, B.P., $C_8H_{10}N_4O_2$, $H_3C_6H_5O_7$); they are decomposed by water.

Test.—Concentrated nitric acid, or, better, a mixture of chlorate of potassium and hydrochloric acid, rapidly oxidizes theine, forming compounds which with ammonia yield a beautiful purple-red colour, resembling the murexid obtained under similar circumstances from uric acid; the oxidation must not be carried too far. Theine boiled with caustic potash yields methylamine (CH_3HHN), the vapour of which has a peculiar, characteristic odour.

The chemical action of theine on the system is not yet quite made out. It is probably a pure stimulant.

THEOBROMINE, $C_7H_8N_4O_2$, is an alkaloid occurring in *cocoa*, the seed of *Theobroma Cacao*, to the extent of 1 to 2 per cent. According to Schmidt, a little theine is present also. Theobromine is also present in Kola-nut (Heckel and Schlagdenhauffen). The theine in cacao and kola and probably that in tea are said to occur normally as glucosides, which would explain why they are only partially extracted by chloroform from a mixture of tea, etc., and lime.

Relations between Theine and Theobromine.—Both theine and theobromine are methyl derivatives of xanthine, $C_5H_4N_4O_2$ (belonging to the uric acid group, uric acid having the formula, $C_5H_4N_4O_3$). Theobromine, or dimethylxanthine, (? the "theophylline" found in tea by Kossel) may be obtained from a compound of xanthine and silver by the action of iodide of methyl; and theine (methyltheobromine, or trimethylxanthine) may be obtained by heating theobromine-silver with iodide of methyl (Strecker).

TRIGONELLINE, $C_7H_7NO_2H_2O$.—Jahns states that this alkaloid, as well as one identical with choline, are present in the seeds of *fænugreek* or *fenugreek* (*Trigonella Fænum-græcum*) much used in veterinary medicine, and in some varieties of cattle food and curry powder.

VERATRINE, or VERATRIA ($C_{32}H_{50}NO_9$, Schmidt and Köppen; $C_{52}H_{86}N_2O_{15}$, Weigelin).—This alkaloid occurs in *Cevadilla* (*Sabadilla*, B.P.; the seeds of *Schænocaulon officinale*, of A. Gray, termed *Asagræa officinalis*, by Lindley, and *Veratrum officinale* by Schlecht). It is also said to occur in the leaves of *Sarracenia purpurea*. According to Weigelin, cevadilla contains two isomeric varieties of veratrine, the one soluble the other insoluble in water. He says there are also present *sabadilline* ($C_{41}H_{66}N_2O_{13}$) and *sabatrine* ($C_{51}H_{86}N_2O_{17}$). The veratrine of trade contains the two latter alkaloids (Weigelin). A mere trace of veratrine brought into contact with the mucous membrane of the nose causes violent fits of sneezing. These alkaloids, and those from the different species of Veratrum, are evidently very closely allied. Wright and Luff, by the use of tartaric acid, a solvent less likely than the stronger acids to decompose alkaloids, extract from cevadilla, *veratrine*, $C_{37}H_{53}NO_{11}$; *cevadine*, $C_{32}H_{49}NO_9$; and *cevadilline*, $C_{34}H_{53}NO_8$. According to Merck, cevadilla contains two alkaloids, *sabadine*, $C_{29}H_{51}NO_8$, and *sabadinine*, $C_{27}H_{45}NO_8$.

The official process for the preparation of the alkaloid (*Veratrina*, B.P.) consists in exhausting the disintegrated cevadilla-seeds by alcohol, recovering most of the spirit by distillation, pouring the residue into water, by which much resin is precipitated, filtering, and precipitating the veratrine from the aqueous solution by ammonia. It is purified by washing with water, solution in dilute hydrochloric acid, decolorization of the liquid by animal charcoal, reprecipitation by ammonia, washing and drying. Bosetti states that

be made with extremely dilute solutions to begin with, say one drop of the solution of the substance under examination to one pint of water. If no effect is produced in an hour, it is easy then to make the experiment with a fluid of double this strength, afterwards with one of twice the latter strength, and so on. The chief dilating agents (mydriatics) are atropine, its isomers and homologues; and the chief contracting agents (myotics) are physostigmine and pilocarpine.

B. If the substance is coloured, seek the aid of the following memoranda :—

1st. If an alkaloid—

Beberine . . .	. Very bitter; soda gives a yellow precipitate, soluble in ether.

2nd. If not an alkaloid—

Aloin	. Very bitter; nitric acid gives a red colour (with soc-aloin brownish). Dissolved in strong sulphuric acid, with addition of a few drops of nitric acid, and diluted with water, it gives an orange or red colour, which is changed to deep claret on addition of ammonia in excess.
Chrysarobin .	. Scarcely soluble in water, soluble in alkalies with fine red colour. Strong sulphuric acid gives red-brown colour.
Jalap Resin .	. See above (may be almost white).
Podophyllin .	. Soluble in alcohol and precipitated by water. Soluble in ammonia and precipitated by acids. Taste slightly bitter.
Santonin . . .	. See above (white when fresh, but yellow after exposure to light).

[*Compiled by F. W. Short.*

To face page 649.]

1. TABLE TO AID IN THE IDENTIFICATION OF OFFICIAL ALKALOIDS, GLUCOSIDES, ETC.

Dissolve a grain or so in a few drops of water, or dilute hydrochloric acid, and add a drop of Mayer's solution (Mercuric Iodide and Iodide of Potassium), or of Iodide of Bismuth and Potassium.

A Precipitate indicates the presence of an Alkaloid.

No Precipitate indicates the absence of an Alkaloid. Search must then be made for glucosides, etc.

A. If the substance is colourless, or nearly so, then :—

To a small quantity on a porcelain plate add strong nitric acid.	Purple-red colour	Apomorphine	Confirm by ferric chloride and by bicarbonate of sodium and chloroform.
	Blood-red ,,	Brucine	,, ,, addition of stannous chloride.
	Orange-red ,,	Morphine	,, ,, ferric chloride and other tests.
	,, ,, ,,	Codeine	,, ,, sulphuric acid and ferric chloride.
	Dirty-red ,,	Veratrine	See next section.
To another portion add strong sulphuric acid.	Red or brown on plate, deep red if warmed in tube.	Veratrine	Confirm by heating with strong hydrochloric acid, which gives a reddish-purple colour.
	Bluish tinge	Codeine	See previous section.
	Blood-red colour	Salicin (glucoside)	Confirm by oxidation.
If not found by preceding sections, heat a little in a dry tube.	Red vapours	Quinine	Confirm by thalleioquin, etc.
		Quinidine	,, ,, ,,
		Cinchonine	,, ,, ether test, etc.
		Cinchonidine	,, ,, ,, ,,

If not found by aid of the preceding sections, test specially as follows :—

1st. If an alkaloid—

Aconitine . . . Make a dilute solution and place a drop on the tongue—numbing and tingling.

Atropine, Homatropine . Alcoholic sol. added to alcoholic sol. of mercuric chloride and warmed = red precipitate. Add nitric acid, dry over water-bath, add alcoholic potash = yellow.

Caffeine . . . Murexid test.

Cocaine . . . Permanganate—purple precipitate. Boiled with potash, then *slightly* acidified with hydrochloric acid and cooled—crystalline precipitate (of benzoic acid).

Physostigmine . Warmed with potash gives red colour which becomes bluish on evaporation to dryness; the residue dissolved in acid gives a dichroic solution.

Pilocarpine . . See page 645.

Strychnine . . Sulphuric acid and red chromate of potassium.

2nd. If not an alkaloid—

Acetanilide . . Heat with potash and chloroform = unpleasant odour of phenyl-isonitrile or phenyl-carbamine, C_6H_5NC.

Elaterin . . . With phenol and strong sulphuric acid, a crimson colour, changing to scarlet.

Gluside (saccharin). Is extremely sweet.

Jalapin (purified Jalap Resin). Insoluble in water or turpentine. Soluble in alkalies or alcohol, partly in ether. Acrid taste.

Phenacetin . . Boil with hydrochloric acid, dilute, cool, filter, add red chromate = deep red.

Phenazone (antipyrin, analgesin). To an aqueous solution add sodium nitrite and diluted sulphuric acid = deep green.

Picrotoxin . . Compare a microscopic slide with one of picrotoxin similarly prepared.

Santonin . . . Almost insoluble in water, but soluble in alkalies. Dilute ferric chloride with an equal volume of strong sulphuric acid gives a red or violet colour.

Sulphonal . . Heat with potassium cyanide (odour of mercaptan); add water, hydrochloric acid and ferric chloride = deep red ($Fe_2 6CNS$).

Note.—Acids are sought by the ordinary reactions carefully applied on small quantities of the substance.

Caution.—Any experiments in which contraction or dilatation of the pupil of the eye is involved should be made with extremely dilute solutions to begin with, say one drop of the solution of the substance under examination to one pint of water. If no effect is produced in an hour, it is easy then to make the experiment with a fluid of double this strength, afterwards with one of twice the latter strength, and so on. The chief dilating agents (mydriatics) are atropine, its isomers and homologues; and the chief contracting agents (myotics) are physostigmine and pilocarpine.

B. If the substance is coloured, seek the aid of the following memoranda :—

1st. If an alkaloid—

Beberine . . . Very bitter; soda gives a yellow precipitate, soluble in ether.

2nd. If not an alkaloid—

Aloin . . . . Very bitter; nitric acid gives a red colour (with soc-aloin brownish). Dissolved in strong sulphuric acid, with addition of a few drops of nitric acid, and diluted with water, it gives an orange or red colour, which is changed to deep claret on addition of ammonia in excess.

Chrysarobin . . Scarcely soluble in water, soluble in alkalies with fine red colour. Strong sulphuric acid gives red-brown colour.

Jalap Resin . . See above (may be almost white).

Podophyllin . . Soluble in alcohol and precipitated by water. Soluble in ammonia and precipitated by acids. Taste slightly bitter.

Santonin . . . See above (white when fresh, but yellow after exposure to light).

[*Compiled by F. W. Short.*

2. TABLE FOR THE QUALITATIVE ANALYSIS OF ORDINARY SCALE COMPOUNDS.

ALKALOIDS.
QUININE. QUINIDINE. BEBERINE.
CINCHONINE. CINCHONIDINE. STRYCHNINE.

Dissolve a portion in water, and add ammonia cautiously. Precipitate = alkaloids (except strychnine) and sometimes ferric hydrate. Agitate the mixture with a little ether and separate, by means of a pipette, the ethereal solution, aqueous solution, and insoluble precipitate.

ETHEREAL SOLUTION.		INSOLUBLE PRECIPITATE.	AQUEOUS SOLUTION.
May contain quinine, quinidine, or beberine. To solution in a test-tube add water very slightly acidulated with acetic acid, boil, burning off the ether. To a portion of the acetic solution add chlorine or bromine water, then ammonia.		Is cinchonine, cinchonidine, or ferric hydrate (red). Saturate a drop or two of acetic acid in a little water with the precipitate, and to part of the solution add tartrate of sodium: a precipitate occurs in the case of *cinchonidine*, and no precipitate in that of *cinchonine*.	May contain strychnine. Agitate with chloroform and separate chloroformic solution. Evaporate chloroformic solution and moisten residue with strong sulphuric acid. Draw across the acid film a small crystal of red chromate of potassium moistened with sulphuric acid, when a transient play of colours—violet to red = *strychnine*. No colours = no strychnine. In case of doubt add ammonia to original solution, agitate with chloroform, and proceed as before.
GREEN COLOUR (thalleioquin).	NO GREEN COLOUR.		
Solution is fluorescent, and contains either quinine or quinidine. Concentrate the remainder of the solution and divide into two parts. To one add iodide of potassium, and to the other add oxalate of ammonium. The former precipitates *quinidine*, not quinine. The latter precipitates *quinine*, not quinidine. For other methods *see* page 625.	To a portion of the acetic solution add potash, a yellowish white precipitate = *beberine*.		

ACIDS.
PYROPHOSPHORIC.
HYPOPHOSPHOROUS (generally converted into pyrophosphoric).
SULPHURIC.
HYDROCHLORIC (as a contamination).
TARTARIC.
CITRIC.

Ignite a small quantity of the scale. Heat the ash with nitric acid, and add to it an excess of solution of ammonium molybdate in nitric acid, and boil.

A YELLOW PRECIPITATE.		NO YELLOW PRECIPITATE.	
Pyrophosphoric or hypophosphorous acid. Precipitate some of the aqueous solution with potash, filter, neutralize with nitric acid, and add nitrate of silver.		Precipitate some of the aqueous solution with potash, filter, and add to a portion of the filtrate a slight excess of nitric acid, divide into two parts. To one add barium chloride (ppt. = *sulphuric acid*). To the other add silver nitrate (ppt. = *hydrochloric acid*). Neutralize another portion of the potash filtrate with nitric acid and add silver nitrate.	
White precipitate soluble in nitric acid = *pyrophosphoric acid.*	White to black precipitate soluble in nitric acid = *hypophosphorous acid.*	PRECIPITATE GREY TO BLACK.	PRECIPITATE WHITE.
		Add very little ammonia (not sufficient to dissolve the whole precipitate) and heat. A silver mirror = *tartaric acid.* Calcium chloride and lime ppt. a neutral solution (if concentrated) in the cold, the precip. redissolving on boiling.	*Citric acid* gives imperfect or no mirror. Calcium chloride and lime do not precipitate citric acid in the cold, but upon boiling (if solution be sufficiently concentrated) precipitation occurs.

Confirm tartaric or citric acid.—To slightly acidified potash filtrate add ammonia in slight excess and considerable quantity of chlorides of ammonium and calcium. *Tartrates* are precipitated completely in the cold with agitation and rest for about ten minutes. To the solution (or filtrate, if tartrates are present) add three volumes of spirit of wine, when *citrates* are precipitated. If sulphates have been found, disregard a slight precipitate with spirit of wine.

INORGANIC BASES.
AMMONIUM (often as a contamination).
FERRIC SALT.
POTASSIUM.
SODIUM.

Ammonium.—Boil aqueous solution of scale with potash and test vapour for ammonia. Filter and dissolve precipitate in hydrochloric acid, and test the solution for *iron* by ferrocyanide, sulphocyanate, etc.

Potassium and sodium.—Ignite a small quantity of the scale, and moisten the residue with water. Test moistened residue with litmus-paper. If alkaline, examine for potassium and sodium by the colour imparted to flame, and for potassium by the platinum test.

[*Table 2. To face p.* 649.]

Compiled by A. SENIER.

it is a mixture of crystalline cevadine, insoluble in water, with an amorphous isomeric soluble alkaloid, *veratridine.* According to Lissauer their physiological action is identical.

Unguentum Veratrinæ, B.P., contains eight grains of the slightly impure alkaloid obtained as just described, rubbed down with one drachm of olive oil, and diffused through one ounce of a mixture of one part of hard and three parts of soft paraffin.

QUESTIONS AND EXERCISES.

How is aconitine prepared?—Give the strength of the official preparations of atropine.—Describe the properties of atropine.—What is the active principle of stramonium?—Mention official substances containing beberine and berberine.—Give the characters of beberine.—In what does nectandrine differ from beberine?—Mention the characteristics of conine.—What is the active principle of ipecacuanha?—Name the alkaloid of tobacco.—Give the properties of the alkaloid of calabar bean. —What are the sources of piperine?—Whence is theine obtained? what is its relation to theobromine?—Describe the preparation of veratrine.—State the properties of veratrine.

HERE THE STUDENT IS RECOMMENDED TO QUALITATIVELY ANALYSE UNNAMED SPECIMENS (PREVIOUSLY SELECTED FOR HIM) OF THE FREE AND COMBINED ORGANIC SUBSTANCES INCLUDED IN THE APPENDED TABLES 1 AND 2.

PROXIMATE CONSTITUTENTS OF ANIMAL ORGANISMS.

Proteid Principles, or Albumenoids.

Albumen.—Agitate, thoroughly, white of egg (*Ovi Albumen*, B.P.) with water, and strain off the liquid from the flocculent membranous insoluble matter. One white to 4 ounces of water forms the "Solution of Albumen," B.P.

Test.—Heat a portion of this solution of albumen to the boiling-point; the albumen becomes insoluble, separating in clots or coagula of characteristic appearance.

Other Reactions.—Add to small quantities of aqueous solution of albumen solutions of corrosive sublimate, nitrate of silver, sulphate of copper, acetate of lead, alum, perchloride of tin; the various salts not only coagulate but form insoluble compounds with albumen. Hence the value of an egg as a temporary antidote in cases of poisoning by many metallic salts, its administration retarding the absorption of the poison until the stomach-pump or other means can be applied. Sulphuric, nitric, and hydrochloric acids precipitate albumen; the coagulum is slowly re-dissolved by aid of heat, a brown, yellow, or purplish-red colour being produced. Neither acetic, tartaric, nor organic acids generally, except picric and gallotannic, coagulate albumen. Alkalies prevent the precipitation of albumen.

Yolk or *Yelk of Egg* (*Ovi Vitellus*, B.P.) contains only 3 per cent. of albumen—the white 12½. The yolk also contains 30 per cent. of yellow fat and 14 of casein, with what is stated to be another proteid, vitellin.

Albumen is met with in large quantity in the serum of blood, in smaller quantity in chyle and lymph, and in the brain, kidneys, liver, muscles, and pancreas. It is not a normal constituent of saliva, gastric juice, bile, or mucus, but may occur during inflammation. It is found in the urine and fæces only under certain diseased states of the system.

The cause of the coagulation of albumen by heat has not yet been discovered.

Albumen has never been obtained sufficiently pure to admit of its composition being expressed by a trustworthy formula; Gerhardt regarded it as a sodium compound ($HNaC_{72}H_{110}N_{18}SO_{22}, H_2O$).

Egg-albumen, and, to some extent, blood-albumen, is largely used by calico-printers as a vehicle for colours, serving also, when dry, as a glaze. Curriers prize egg-oil for softening leather.

Albumen coagulated by heat is said to be recoverable in a scarcely altered fluid condition by contact with a dilute aqueous solution of a very small proportion of pepsin.

Fibrin, Casein, Legumin.

Fibrin is the chief constituent of muscular tissue. It occurs in the blood in the form of a very unstable compound termed *fibrinogen*; and its liberation from this union and spontaneous solidification or coagulation is the cause of the *clotting* of blood shortly after being drawn from the body. The latter phenomenon cannot at present be explained satisfactorily. Fibrin may be obtained by whipping fresh blood with a bundle of twigs, separating the adherent fibres, and washing in water till colourless. It may be kept either dry or in spirit of wine.

Average Composition of Blood (in 1,000 parts).
(Compiled by Kirkes.)

	Water		784
	Albumen		70
	Fibrin		2·2
	Red corupscles (globulin, 123 ; hæmatin, 7)		130
Fatty Matters.	Cholesterin	0·08	1·4
	Cerebrin	0·40	
	Serolin	0·02	
	Oleic and margaric acids		
	Volatile and odorous fatty acid		
	Fat containing phosphorus		
Inorganic Salts.	Chloride of sodium		3·6
	Chloride of potassium		·35
	Phosphate of sodium (Na_3PO_4)		·2
	Carbonate of sodium		·82
	Sulphate of sodium		·28
	Phosphates of calcium and magnesium		·25
	Oxide and phosphate of iron		·50
	Extractive matters, biliary colouring-matter, gases, and accidental substances		6·4
			1000·0

Percentage Proportion of the *Chief* Constituents of Blood.

Water	78·4
Red corpuscles (solid residue)	13·0
Albumen of serum	7·0
Inorganic salts	·6
Extractive, fatty and other matters	·8
Fibrin	·2
	100·0

Casein occurs in Cow's Milk (*Lac*, B.P.) to the extent of about 4 per cent., dissolved by a trace of alkaline salt. Its solution does not spontaneously coagulate, like that of fibrin, nor by heat like albumen ; but acids cause its precipitation from milk in the form of a curd (cheese) containing the fat-(butter-) globules previously suspended in the milk, a clear yellow liquid (or whey) remaining. *Curds and whey* are also produced on adding to milk a piece, or an infusion, of *rennet*, the salted and dried inner membrane of the fourth stomach of the calf. The exact action of rennet is not known, but it seems to be due to the presence of a milk-curdling ferment which is not an acid, and not pepsin, and which appears also to occur in the pancreatic juice, the intestinal juice, and some vegetable juices. Respecting rennet Soxhlet says: "60 to 80 grammes of calf's stomach steeped for five days in 1 litre of a 5-per-cent. solution of common salt at ordinary temperatures, yield a solution of which 1 vol. will coagulate 10,000 vols. of new milk at a temperature of 95° F. in forty minutes. If the filtered solution is treated with 60 to 90 grammes more of stomach, a solution of double strength is obtained; another repetition gives a solution three times the strength of the original one. To prevent decomposition, about 0·3 per cent. of thymol may be added to the concentrated rennet extract solution. Possibly a slight taste due to this may be detected in the finest cheese, but for the same reason oil of cloves is much more objectionable. Boric acid is on all accounts the best antiseptic to employ, and solutions to which it has been added may be kept in covered vessels for months. All extract-solutions lose strength on keeping; during the first two months the solution may become 30 per cent. weaker, then the strength remains nearly constant for eight months in the case of a solution of 1 in 18,000. Alcohol is almost as good an antiseptic as boric acid, if the solution be preserved in well-stoppered flasks."

Average Composition of 1,000 parts of Milk.

	Specific gravity.	Water.	Solid constituents.	Casein and extractive.	Sugar.	Butter.	Salts.
Woman .	1·030 to 1·034	870	130	27	60	40	3
Cow . .	1·030 to 1·035	877	123	40	46	30	7

Leeds put the average composition of human milk at 2 per cent. of albumenoids, 7 per cent. of milk sugar, 4 per cent. of fat and 0·2 per cent. of ash.

Specific gravity alone, as taken by the form of hydrometer termed a *lactometer*, or even by more delicate means, is of little value as an indication of the richness of milk, the butter and the other solids exerting an influence in opposite directions. Good cow's milk affords from 10 to 12 per cent. by volume of cream, and 3 to 3½ per cent. of butter. The water of milk seldom varies more than from 87 to 88 per cent., and the solid constituents from 13 to 12. Indeed, excluding its butter, milk is curiously regular in composition. The non-fatty solids in the mixed milk of a herd or dairy of healthy cows is almost a constant quantity, namely 9·3 per cent. A lower proportion of non-fatty solids in a sample of milk points to the addition of water. Thus, supposing that 100 grains of a specimen of milk evaporated to dryness, and all butter extracted from the residue (previously disintegrated by help of 1 or 2 parts of dried gypsum, or the dried infusorial earth termed *Kieselguhr*) by ether (or placed on blotting paper and dried and exhausted by ether—Adams), yielded a non-fatty residue of 7·44 grains, the specimen would probably be four-fifths milk and one-fifth water.* For if 9·3 indicate 100, then 7·44 indicate 80. Occasionally, under exceptional circumstances, a sample of genuine milk might be slightly poorer than that from a healthy herd, and therefore, for legal purposes, a standard of 9 per cent. by weight of non-fatty solids and 2·5 per cent. of butter-fat has been proposed. Only in the rare cases of milk containing an unusually large proportion of butter-fat would any milk yielding less than 9 per cent. of non-fatty solids be regarded as genuine. And, again, no milk would be considered genuine, under this standard, if it yielded less than 2·5 per cent. of fat, not even in the rare case of its containing an unusually large proportion of real non-fatty milk-solids. Half-starved cows might yield milk below these standards; but it could scarcely be considered to be normal, or better fitted for food than milk watered *after* leaving the cow. If, however, such milk is to be regarded as genuine, the standard of 8·5 of non-fatty solids will not be too low.

Ewe's milk is much richer than either human or cow's milk.

Under the microscope milk is seen to consist of minute corpuscles floating in a transparent medium. Those corpuscles consist of the fatty matter (butter), said to be contained in a filmy albumenoid envelope. The fat is fluid at the normal temperature of the animal, and remains so until the milk is well agitated by churning or otherwise, or until the milk is frozen.

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* Soxhlet determines fat by noting the specific gravity of an ethereal solution and then referring to tables showing percentage of fat in ethereal solutions of varying specific gravity.

Legumin, or *vegetable casein*, is found in most leguminous seeds, and in sweet and bitter almonds. Peas contain about 25 per cent. of legumin.

Vegetable albumen is contained in many plant-juices, and is deposited in flocculi on heating such liquids. *Vegetable fibrin* is the name given by Liebig and Dumas to that portion of the gluten of wheat which is insoluble in alcohol and ether. *Spongine*, the organic matter of sponge, appears to be a proteid.

Albumenoid substances are nearly identical in percentage composition. Albumen and fibrin contain 53·5 of carbon, 7 of hydrogen, 15·5 of nitrogen, 22 of oxygen, 1·6 of sulphur and 4 of phosphorus. Casein contains no phosphorus. These three bodies Liebig termed the *plastic elements of nutrition*, under the assumption that animals directly assimilate them in forming muscles, nerves and other tissues,—starch, sugar and similar matter forming the *respiratory* materials of food, because more immediately concerned in keeping up the temperature of the body by the combustion going on between them, and their products, and the oxygen of the air in the blood; but the classes are scarcely so well differentiated as the terms would imply.

The whole of the organic nitrogen in food must not moreover be regarded as representing true albumenoids, some existing as amidic and similar compounds, bodies having a simplicity of composition characteristic of the *products* of physiological action on food, rather than that complexity of composition characteristic of true nutrients. Albumenoids in decomposing yield much fatty matter as well as other substances. Possibly a portion, at least, of the *adipocere* (*adeps*, fat; *cera*, wax), or *corpse-fat*, characteristic of the remains of buried animals, is thus derived.

Albumenoids are divided, according to their solubility in water and certain saline solutions such as ammonium sulphate, into "albumens" or "albumins" "globulins" "albumoses" "peptones," etc. To the second of these classes the poisons of most venomous snakes probably belong, and a globulin and an albumose, each harmless when swallowed, but extremely poisonous when injected into the blood, occur in the seeds of *Abrus precatorius* (Jequirity).

Musk (*Moschus*, B.P.)., "the dried secretion from the preputial follicles of *Moschus moschiferus*" (the Musk-deer), is a mixture of albumenoid, fatty, and other animal matters with a volatile odorous substance of unknown composition. "Artificial Musk" a synthetical compound having an odour resembling in quality and power that of natural musk, is trinitro-isobutyl-toluene C_6HCH_3, $C(CH_3)_3$,$(NO_2)_3$.

GELATIGENOUS SUBSTANCES.

These nitrogenous bodies differ, chemically, from the albumenoid in containing less carbon and sulphur and more nitrogen. They are contained in certain animal tissues, and on boiling with water yield a solution which has the remarkable property of solidifying to a jelly on cooling. The tendons, ligaments, bones, skin, and serous membranes afford *gelatine* proper; the cartilages give *chondrine*, which differs from gelatine in composition and in being precipitatod by vegetable acids, alum, and the acetates of lead. The purest source of gelatine is *isinglass* (B.P.), "the swimming-bladder or sound of various species of *Acipenser*, Linn., prepared and cut in fine shreds." Small quantities are more easily disintegrated by a file than a knife. Fifty grains dissolved in 5 ounces of distilled water forms the official "Solution of Isinglass," B.P. Gelatine (*Gelatinum*, B.P.) is officially defined as "the air-dried product of the action of boiling water on gelatigenous animal tissues, such as skin, tendons, ligaments, and bones." *Glue* is an impure variety of gelatine, made from the trimmings of hides; *size* is glue of inferior tenacity, prepared from the parings of parchment and thin skins. "Among the varieties of gelatine derived from different tissues and from the same sources at different ages, much diversity exists as to the firmness and other characters of the solid formed on the cooling of the solutions. The differences between isinglass, size, and glue, in this respect, are familiarly known, and afford good examples of the varieties called weak and strong, or low and high gelatines. The differencos are sometimes ascribed to the quantities of water combined in each caso with the pure or anhydrous gelatine, part of which wator soems to be intimatoly united with the gelatino; for no artificial addition of wator to gluo would give it tho character of sizo, nor would any abstraction of water from isinglass or size convert it into the hard dry substance of glue. But such a change is effected in the gradual process of nutrition of the tissues; for, as a general rule, the tissues of an old animal yield a much firmer or stronger jelly than the corresponding parts of a young animal of the same species." (Kirke's Physiology.)

Gelatine is supposed by some to be a glucoside, yielding an ammonium salt when boiled with diluted acids. It appears to unite chemically with a portion of the water in which it is soaked when used for culinary or manufacturing purposes, for a solution of glue in hot anhydrous glycerine does not yield an ordinary jelly on cooling. From its solution in water, gelatine is precipitated by alcohol, corrosive sublimate, perchloride of platinum, and by tannic acid. Its aqueous solution is not, like that of albumen, coagulated by heat, nor is it precipitated by acids. By prolonged ebullition its gelatinizing power is destroyed.

PEPSIN.

Pepsin (from πέπτω, *pepto*, I digest) is a nitrogenous substance existing in the gastric juice, and as a viscid matter in the *peptic* glands and on the walls of the stomachs of animals. It appears to be a modification of a precursor termed *propepsin*, stomachs not yielding so much pepsin when quite fresh as after twenty-four hours. To isolate pepsin, the cleansed mucous membrane of the stomach (of the hog, sheep, or calf, killed fasting) is scraped, and macerated, with the scrapings, in cold water for twelve hours; the pepsin in the strained liquid is then precipitated by acetate of lead, the deposit washed once or twice by decantation, sulphuretted hydrogen passed through the mixture of the deposit with a little water to remove the whole of the lead, and the filtered liquid evaporated to dryness at a temperature not exceeding 105° F. Pepsin is a powerful promoter of digestion; its solution is hence frequently termed *artificial gastric juice*. As met with in pharmacy, its strength varies greatly. It is often prepared by simply mixing with starch the thick liquid obtained on macerating the scraped stomach with water, and evaporating to dryness. (*Vide Pharmaceutical Journal*, 1865–66, p. 112, and 1871–72, pp. 785 and 843.) The official process (*Pepsin*, B.P.) simply consists in scraping the viscid pulp from the slightly washed inner surface of the stomach and quickly evaporating it to dryness on glass or glazed earthenware at a temperature not exceeding 100° F. The product is powdered. "A light yellowish-brown powder, having a faint but not disagreeable odour, and a slightly saline taste, without any indication of putrescence. Very little soluble in water or spirit. Two grains of it, with an ounce of distilled water, to which 5 minims of hydrochloric acid have been added, form a mixture in which at least 100 grains of hard-boiled white of egg, passed through wire gauze of 36 meshes per linear inch, and made of No. 32 brass or copper wire, will dissolve on their being well mixed, digested and well stirred together for thirty minutes at a temperature of 130° F. (54·4° C.)." The solvent or digestive action of pepsin on the albumenoids, etc., in the stomach results in a nutritive and digestive fluid termed *peptone*, forming a portion of the whole product of stomach-digestion or *chyme*. It is thus that such food is prepared for conversion into blood. Artificial or alimentary peptone may be made by digesting blood fibrin with pepsin in very weak hydrochloric acid. Clermont prepares alimentary peptone in solution by heating 40 parts of minced meat with 30 of water and 1 of sulphuric acid in a sealed tube, filtering and evaporating the rosulting fluid to dryness and treating the residue with water. The solution is not precipitated by hydrochloric, acetic, or nitric acid; when diluted with strong 90-per-cent. alcohol, it gives an abundant precipitate; and it is precipitated by tannin, mercuric chloride, and platinic chloride. Peptone is not readily coagulated by heat, and it freely diffuses through membranes. It appears to be isomeric with albumen. *Propeptone*, *para-peptone*, or *hemialbumose*, is a mixture of substances intermediate betwoen albumen and peptone. It readily diffuses through membranes. Some vegetables, notably the leaves of the papaw tree, *Carica papaya*, appear to contain a principle, "papain," analogous in properties to pepsin. According to Wurtz, papain is an albumenoid.

(For a *résumé* of the modes of preparing pepsin, *see* an article by Petit in the *Pharmaceutical Journal* for July 17, 1880.)

PANCREATIN.

The pancreas (or "sweetbread") secretes a colourless fluid which contains $1\frac{1}{2}$ to $2\frac{1}{2}$ per cent. of an albumenoid substance, which has the power of converting starch into sugar and, especially, of emulsifying fat. It may be precipitated by chloride of sodium from an acidulated infusion of the pancreas. Stutzer obtains a powerful extract by digesting the pancreas in lime-water and glycerine with free exposure to air. It is soluble in cold water. An extremely small proportion emulsifies a large volume of fat. The pancreatic juice would seem to contain four distinct ferments, namely, the *emulsifying principle*, the *milk-curdling ferment*, *pancreatic diastase*, and a pepsin-like substance termed *trypsin*, which, unlike pepsin, attacks albumenoids in neutral or even slightly alkaline fluids.

Bile.

The *gall* or *bile* of the ox (*Bos taurus*, Linn.), evaporated to one-fourth of its bulk and freed from mucus by agitating with twice its bulk of rectified spirit (in which mucus is insoluble), filtering and evaporating, yields the official Purified Ox-Bile (*Fel Bovinum Purificatum*, B.P.): the latter has the appearance of a yellowish-green soft resin, but is chiefly composed of two crystalline substances having the constitution of a soap; the one is termed *taurocholate of sodium* ($NaC_{26}H_{44}NO_7S$), the other is *glycocholate*, or simply *cholate*, *of sodium*, ($NaC_{26}H_{42}NO_6$). Both taurocholates and glycocholates are conjugated bodies readily yielding, the former *cholic* or *cholalic acid* ($HC_{24}H_{39}O_5$) and *taurine* ($C_2H_7NO_3S$), the latter cholalic acid and *glycocine* or *glycocoll* or *amidacetic acid* $CH_2(NH_2)COOH$, a soluble crystalline body having interesting physiological relations, for it is obtainable from gelatine (hence the name glycocoll or sugar of gelatine, from γλυκὺς, *glucūs*, sweet, and κόλλα, *kolla*, glue) and from hippuric acid. Choline ($C_5H_{15}NO_2$) is an alkaloid originally found in bile, hence its name (χολή, *cholē*, bile), but it occurs in the brain, etc., in cod-liver oil, and in plants—ergot, Indian hemp, ipecacuanha, etc. (*Vide* Index, "Choline.")

Tests for Bile.—The presence of bile in a liquid, such as urine, may be detected by the following tests. The fluid is gradually mixed with half its bulk of strong sulphuric acid in a test-tube, rise of temperature being prevented by partial immersion of the tube in water. A small quantity of powdered white sugar is then introduced and well mixed with the acid liquid, and more sulphuric acid then poured in;

as the temperature rises, a reddish or violet coloration is produced. The cholalic acid liberated in the reaction furnishes the colour. This is Pettenkofer's test. It is somewhat interfered with by albumen and volatile oils. Quinlan tests for bile by placing a three-millimetre stratum of the suspected fluid before the slit of the spectroscope, and observing the absorption, which extends, according to the amount present, from the violet of the spectrum to the Fraunhöfer line D.

QUESTIONS AND EXERCISES.

In what form is albumen familiar?—Name the chief tests for albumen. —Why is the administration of albumen useful in cases of poisoning?—Mention the points of difference between yolk and white of egg.—From what sources other than egg may albumen be obtained?—In what respects does fibrin differ from albumen?—Enumerate the chief constituents of blood.—How may fibrin be obtained from blood?—State the difference between casein, fibrin and albumen.—What are the relations of cream, butter, curds and whey, and cheese to milk?—Describe the microscopic appearances of blood and milk.—How much cream should be obtained from good milk?—What is the percentage of water in genuine milk?—Name the sources of vegetable albumen and vegetable casein.—Give the percentage of nitrogen in albumenoid substances.—Describe the chemical nature of musk.—In what lie the peculiarities of gelatigenous substances?—To what extent do isinglass, glue, and size differ?—Whence is pepsin obtained, and how prepared?—Give the proximate constituents of bile.—What are the tests for bile?

COLOURING MATTERS.

The animal, vegetable, and mineral kingdoms abound in substances or pigments which powerfully decompose light, absorbing certain of its constituent colours, and reflecting the others. Thus, for example, most leaves contain a body termed chlorophyll, which has the property of absorbing red light and reflecting green; these reflected rays entering the eye of an observer, and striking on the retina (the expanded extremity of the optic nerve), always communicate the same impression to the brain; in popular language the leaf is said to be green. Art has richly supplemented the number of such natural colouring matters.

Yellow.—1. *Chrome yellow* occurs in more than a dozen shades (*see* Lead, chromate of). 2. *Fustic* or *yellow wood* is the wood of the *Rhus Cotinus*. 3. *Gamboge* (*see* Gamboge). 4. *Ochre* is met with of many tints, under the names of *yellow ochre*, *gold yellow*, *gold earth* or *ochre*, *yellow sienna*, *Chinese yellow*. It is chiefly a mixture of oxyhydrates of iron with alumina and lime. It has been used from the earliest times. 5. *Orpiment* is a sulphide of arsenium (As_2S_3). 6. *Persian berries*, or *Avignon grains*, contain a yellow principle termed *rhamnin* and other crystalline bodies; they are the product of two or three species of *Rhamnus*. 7. *Purree*, or *Indian yellow*, is said by Stenhouse to owe its colour to *purrate* or *euxanthate of magnesium* ($MgC_{42}H_{34}O_{22}$). 8. *Quercitron* is the bark of *Quercus tinctoria*: it contains the yellow glucoside, *quercitrin* ($C_{36}H_{38}O_{20}$). 9. *Rhubarb* (*see* Chrysophanic acid, p. 399). 10. *Saffron* (*Crocus*, B.P.), the dried stigma and part of the style of *Crocus sativus*, yields *saffranin* or *polychroite*, an orange-red glucoside, which, by the action of dilute acids and by other means, breaks up as shown in the following equation, yielding red *crocin* (Weiss).

$$\underset{\text{Polychroite.}}{C_{48}H_{60}O_{18}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Crocin.}}{2(C_{16}H_{18}O_6)} + \underset{\text{Vol. oil of saffron.}}{C_{10}H_{14}O} + \underset{\text{Sugar.}}{C_6H_{12}O_6}.$$

Kayser, however, gives the formula of pure crocin as $C_{44}H_{70}O_{28}$, and states that by absorption of water, $7H_2O$, it yields pure *crocetin*, $C_{34}H_{46}O_9$, and sugar, $9C_6H_{12}O_6$. Any admixture of carbonate of calcium, sulphates of barium or calcium, or similar powder, with saffron, is readily detected on placing a little in a glass of warm water, and stirring; when insoluble powder is deposited. "Ignited with free access of air, it should yield not more than 6 per cent. of ash" (B.P.). 11. *Turmeric*, the rhizome of *Curcuma longa*, owes its yellow colour to *curcumin*, a resin, the formula of which is said by Daube to be $C_{10}H_{10}O_3$, and by Iwanof, $C_{16}H_{16}O_4$. Jackson and Monke state that curcumin is an acid, and that its formula is $H_2C_{14}H_{12}O_4$. Apparently two yellow pigments are present. The colouring-matters of turmeric are readily dissolved by chloroform, not so those of saffron, mustard, or the best East-Indian rhubarb, on which fact methods of detecting turmeric in those substances have been founded. (Howie, *Pharmaceutical Journal*, November 1, 1873.) 12. *Weld* (*Reseda luteola*) contains a durable yellow matter termed *luteolin* ($C_{20}H_{14}O_3$). 13. *Picric* or *carbazotic acid* (p. 541) is a very powerful yellow dye. 14. Dried and powdered carrots yield to bisulphide of carbon a yellow colouring-matter, "carrotin," which is obtained on evaporating the solvent. It is said to be used in colouring butter.

RED.—1. *Alkanet*, the root of *Alkanna tinctoria*, Tausch, *Anchusa tinctoria*, Desf., yields *anchusin* ($C_{35}H_{40}O_8$), a resinoid matter soluble in oils and fat. 2. *Annatto*, *arnatto*, or *arnotto*, a paste prepared by evaporating a strained aquoous extract of the seeds of *Bixa Orellana*, contains *bixin* ($C_{28}H_{34}O_5$) an orange-red, and *orellin* a yellow principle. 3. *Brazil-wood* (*Cæsalpinia Brasiliensis*) furnishes *brezilin*, $C_{16}H_{14}O_5$, the basis of several lakes; *sapan-wood* and *camwood* probably contain the same substance. 4. *Cinnabar*, Chinese red, Vermilion, or Paris red, is mercuric sulphide. It is a very ancient red pigment. 5. *Chrome-red* is an oxychromate of lead. 6. *Cochineal* (p. 398). 7. *Madder*, the root of *Rubia tinctoria*, powdered and treated with sulphuric acid and acidulated water to effect the removal of earthy and other inert matters, furnishes a residual powder termed *garancin*. Garancin yields to pure water *alizarin* ($C_{14}H_{10}O_4, 3H_2O$), the red, neutral, crystallizable colouring-matter of madder. Alizarin does not exist ready formed in the plant, but is derived, by fermentation, from a glucoside, termed *rubianic acid*. Alizarin is now largely produced artificially from *anthracene*, one of the solid constituents of coal-tar (*see* p. 518). 8. *Mulberry-juice* (*Mori Succus*, B.P.) contains a violet-red colouring-matter which has not been chemically examined. 9. *Red lead* (p. 243). This and the following ochre are very ancient red colouring-matters. 10. *Red oxide of iron*, of shades varying from light to brown-red, is found native The common names of it are Armenian bole, Berlin red, colcothar, English red, red ochre, burnt ochre, red earth, terra di sienna, mineral purple, stone-red, and Indian red. 11. *Red sanders-wood* or *Red sandal-wood* or *barwood* (*Pterocarpi Lignum*, B.P.) the billets and chips of *Pterocarpus santalinus*, owes its colour to *santalin* ($C_{14}H_{12}O_4$), a crystalline resinoid matter. Crystalline *pterocarpin*, $C_{10}H_8O_3$, and *homopterocarpin*, $C_{12}H_{12}O_3$, are also present (Cazeneuve). 12. *Red-Poppy Petals* (*Rhœados Petala*, B.P.), from the *Papaver Rhœas*, contain a red colouring principle which has not yet been isolated in a state of purity. The author has sought for morphine in large quantities of the petals, but could not find a trace of that alkaloid. 13. *Red-Rose Petals* (*Rosæ Gallicæ Petala*, B.P.), and those of the Cabbage-Rose (*Rosæ Centifoliæ Petala*, B.P.), also yield a red substance which has not been analysed. 14. *Safflower*, *dyer's saffron*, or *bastard saffron*, the florets of *Carthamus tinctorius*, contains an unimportant yellow dye, and 5 per cent. of *carthamin* ($C_{14}H_{16}O_7$), an uncrystallizable red dye, the pigment of the old *pink saucers*. Carthamin seems to possess acid characters, and (like silicic acid and other substances) to be soluble in water for a certain time after liberation from its alkaline solution; for fabrics are dyed with safflower by immersion in a bath made of an infusion in dilute alkali neutralized by citric acid immediately before use, the carthamin probably penetrating the cells and vessels of the fibres in a soluble form, there becoming insoluble and imprisoned, and thus giving permanent colour to the wool, silk, or other material. Mixed with French chalk, carthamin is used as a cosmetic under the name of *vegetable rouge*—*carmine* being *animal rouge*, and *red oxide of iron* the *mineral rouge*. 15. *Lac-dye* is a cheap form of cochineal, and is also yielded by the species of *Coccus* whose resinous excretion constitutes *lac* (*stick-lac*, *seed-lac*, or *shell-lac*, according to its condition as gathered off the twigs on which it is deposited, or as roughly separated from impurities in seed-like powder or lumps, or as melted and squeezed through bags into shell-like pieces). 16. *Logwood* (*Hæmatoxyli Lignum*, B.P.) contains a yellow substance, *hæmatoxylin* ($C_{16}H_{14}O_6,H_2O$ or $3H_2O$), to which any medicinal usefulness of the wood is perhaps due, and which, under the influence of air and alkali or ferments, assumes a very intense red colour—*hæmatein*. Under the influence of ammonia and air also hæmatoxylin yields greenish-violet iridescent scales of this *hæmateïn* ($C_{16}H_{12}O_6 3H_2O$). 17. *Red enamel* colours, for glass-staining and ceramic operations, are produced either by cuprous silicate or purple of Cassius (p. 285).

BLUE.—1. *Cobalt oxide* precipitated in combination or admixture with alumina or phosphate of calcium forms *Thénard's blue*, *cobalt-blue*, *Hoffner's blue*, and *cobaltic ultramarine*. 2. *Smalt*, *Saxony blue*, or *King's blue* is rough cobalt glass in fine powder (p. 269). 3. *Copper-blue*, *mountain-blue*, and *English* or *Hambro' blue* are chiefly oxycarbonates of copper. 4. *Indigo*, $C_{16}H_{10}N_2O_2$, Sommaruga (p. 339). 5. *Litmus*, *lichen-blue*, *turnsole*, *orchil* or *archil*, and *cudbear*, are products of the action of air and alkalies on certain colourless principles, as *orcin* ($C_6H_3(OH)_2CH_3$), derived from different species of lichen—*Roccella*, *Variolaria*.

and *Lecanora.* 6. *Prussian blue* (p. 403) and *Turnbull's blue* (p. 404) are met with under the names of *Erlangen*, *Louisa*, *Saxon*, *Paris*, or *Berlin blue.* 7. *Ultramarine*, a very old blue pigment, formerly obtained from the rare mineral, *lapis lazuli*, is now cheaply made on a large scale by roasting a mixture of fine white clay, carbonate of sodium, sulphur and charcoal or rosin. Its constitution is not well made out. Acids decompose it, sulphuretted hydrogen escaping.

PURPLE.—*See* Murexid, p. 428.

GREEN.—1. *Cupro-arsenical* green pigments (page 200). Most of the ancient greens contain carbonate of copper. The old *emerald green* is a hydrous oxide of chromium, but aceto-arsenite of copper is now sold under this name. 2. *Chlorophyll*, *leaf-green*, or *chromule.* A method of extracting chlorophyll is given under "Extracts" (*vide* Index). It is resinoid, soluble in alcohol and ether, insoluble in water, and, according to Frémy and to Schunck, consists of a blue substance, *phyllocyanin*, ($C_{34}H_{68}N_4O_{17}$?), and a yellow, *phylloxanthin ;* the yellow tints in fading autumnal leaves, he says, are due to the latter principle, the former being the first to fade. Chlorophyll would probably well repay extended investigation, as it has never been obtained pure. 3. *Sap-green*, *buckthorn-*, *vegetable-*, or *bladder-green*, known also as *Chinese green*, or *lokas*, is obtained by evaporating to dryness a mixture of lime and the juice (*Rhamni Succus*, B.P., 1867) of the berries of buckthorn (*Rhamnus catharticus*). It is soluble in water, slightly in alcohol, and insoluble in ether and oils. 4. *Green ultramarine* is made by a process similar to that for blue ultramarine. 5. Mixtures of blue and yellow pigments and dyes are common sources of green colours. 6. Glass and earthenware are coloured green by oxide of chromium and black oxide of copper.

BROWN.—1. *Umber*, *sienna*, or *chestnut-brown* is found native. By heat it is darkened in tint, and is then known as *burnt umber*. It is a mixture of oxide of iron, silica, and alumina. 2. *Sepia* is a dried fluid from the ink-bag of cuttle-fishes (*Sepiadæ*); by its ejection into adjacent water the animal is said to obtain opportunity of escape from enemies. 3. *Catechu* (p. 424) furnishes a brown colouring-matter.

BLACK.—1. *Blacklead* (p. 22), *bone-black* (p. 122), or *ivory-black* and *lamp-black*, the latter a deposited soot from the incomplete combustion of resin and tar, are varieties of carbon. 2. *Burnt sugar*, or *caramel* (p. 561). 3. *Indian ink* is usually a dried mixture of fine lampblack and size or thin glue. 4. *Black ink* is essentially tannates and gallates of iron suspended in water containing a little gum in solution. 5. *Printer's ink* is well boiled linseed or other oil, mixed with good lampblack, vermilion, or other pigment. 6. *Black dyes* are of the same nature as ink. 7. The old "*pigmentum nigrum*" of black feathers, such as those of the common rook, of dark hair, and probably also of the skin of the negro, is, doubtless, the black substance which remains undissolved when black feathers are digested for some time in dilute sulphuric acid. It is said to have the formula $C_{18}H_{16}N_2O_8$ (Hodgkinson and Sorby.)

WHITE PIGMENTS.—1. *Chalk* or *whiting* (p. 121). 2. *French chalk*, *steatite*, or *soapstone*, is largely silicate of magnesium. 3. *Heavy white* (p. 112). 4. *Pearl-white* (p. 292). 5. *Plaster of Paris* (p. 114). 6. *Starch* (p. 563). 7. *White lead* or Cremnitz white (p. 241). 8. *Zinc white* or *Chinese white* (p. 149). 9. "*Constant*" *white* is tungstate of barium. 10. *Flake white* is basic nitrate of bismuth. 11. Oxides of tin and zinc and phosphate of calcium are employed for giving a white opacity to glass.

ANILINE COLOURS. *Coal-tar colours.*—Within the last ten years nearly every shade of colour seen in the animal and vegetable kingdoms has been successfully imitated by certain dyes and pigments primarily derived from a mineral, coal. Coal distilled for gas furnishes tar or gas-tar. Coal-tar contains some aniline; but especially it contains a liquid convertible into aniline, namely benzene (C_6H_6), first discovered by Faraday in compressed oil-gas. From aniline, by oxidation, Runge obtained the violet-colour reaction, the body producing which Perkin afterwards studied and isolated, and manufactured under the name of *mauve*. *Aniline-red* (*fuchsine*, *magenta*, or *rosaniline*), *aniline-yellow*, *aniline-green*, *aniline-blue*, and, in short, aniline-dyes, lakes, and pigments of every hue of the rainbow, are now common articles of trade. Their application has revolutionized the arts of the dyer and colour-printer. Some of the coal-tar colours are not "aniline" colours, being derived from naphthalene, phthalic acid, phenol, etc.

QUESTIONS AND EXERCISES.

Explain the production of colour by the various natural and artificial pigments.—Mention the chief yellow colouring-matters, and describe their chemical nature—What is annatto?—Name the colorific constituent of madder. Can it be made artificially?—State the source of litmus?—Distinguish between Prussian blue and Turnbull's blue; and state how they are manufactured.—How is blue ultramarine obtained? How is it affected by acids?—Describe the chemical nature of the colouring principles of leaves.—By what agents is glass coloured green?—Whence is sepia obtained?—Describe the chemistry of black ink.—Write a few sentences on *aniline colours.*

QUALITATIVE ANALYSIS OF SUBSTANCES HAVING UNKNOWN PROPERTIES.

Substances are presented to the analyst in one of the three forms in which all mattor exists—namely, solid, liquid, or gaseous; and they may contain animal or vegetable as well as mineral matter.

The method of analysis in the case of *solid mineral bodies* has been described on pp. 438 to 448.

Solid animal or vegetable substances (or mixtures of these with mineral bodies) may be indefinite and beyond the grasp of chemistry, or definite and quite within the range of proximate qualitative organic analysis. The presenco of such substances is indicated in the preliminary examination of a solid (pp. 439 to 442) by charring and other characters. If no charring occurs, and no volatile liquid is expelled by heat, the absence of such matter is indicated. But if organic matter is present, an endeavour is made to ascertain its precise character. The analyst's knowledgo of the history of the substance, or the circumstances undor which it comes into his hands, will probably afford a clue to its nature, and enable him to search directly for its proximate constituents. If no such information is at hand, the action of solvents may be employed, as likely to afford indication of the general, if not of the precise, naturo of the substance. Water, alcohol, ether, chloroform, bisulphide of carbon, each hot and cold, may in turn be agitated with the substance, tho mixture be filtered, a portion of the filtrate ovaporated, at first partially, setting the product aside, and afterwards to drynoss, and any deposit or residue be examinod with and without the aid of a microscope. Othor portions of tho filtrato may be treated with acids, alkalies, and solutions of such metallic salts as are commonly used as group-tests for acidulous radicals (p. 437). The action of alkalies, as well as acids, weak and strong, hot and cold, may also be tried on the solid substance itself, and colours, odours, and, in short, any effect whatever, be duly noted. A portion of the substance should also be burnt in an open porcelain crucible until no carbon remains, and the ash, if any, be examined; its amount and nature may afford information leading to the identification of the substance.

The foregoing experiments having been carefully performed, and all results entered in the note-book, a little reflection will possibly lead to recognition, or may suggest further direct experiments or confirmatory tests, or will, at least, have pointed to the absence of 90 or 95 per cent. of all possible substances, and thus have restricted the area of inquiry to narrow limits. The success attainable in qualitative proximate organic analysis by the medical or pharmaceutical student will of course largely depend on the thoroughness with which the operator has prosecuted his study of practical chemistry generally; but it also will be considerably affected by the extent to which he has cultivated the art of observation, and the opportunities he has had of acquiring a knowledge of the appearance, uses, and common properties of definite chemical substances, and of articles of food, drink, and medicine. The most successful of several good analysts will be the one who has most common sense and most experience.

The pharmaceutical student, who has probably already had some years of experience in pharmacy, occupies an unusually favourable position for prosecuting the proximate analysis of organic and inorganic substances, or, at all events, of that large proportion of such bodies met with in the domain of hygiene and pharmacy. Many substances he will identify at sight, or by aid of a lens, or after applying some simple physical or chemical test. Nor should he find much difficulty, after reaching the present point of practical study, in deciding whether the solid substance under examination belongs to the class of organic acids, organic salts of metallic radicals, alkaloids, salts of alkaloids, amylaceous matter, gums, saccharine substances, glucosides, albuminoid matters, fats, soaps, rosins, colouring-matters, etc. For instance, the pharmaceutical student will find less difficulty than the general student in successfully analysing a substance occurring in "scales," because he has experience of the appearances of compounds commonly produced in that form, and because, even if the appearance is new to him, he knows what kind of substances most readily lend themselves to production in that form. While the general student is testing generally, and proceeding cautiously, or searching for general information in books of reference, the pharmaceutical or medical student has incinerated some of the material, noticed whether or not the ash is red (iron) and strongly alkaline (potassium), treated more of the material with an alkali (for ammonium), added excess of ammonia, and examined the precipitate (for cinchonine or quinine) or shaken up the alkaline liquid successively with ether and chloroform, and tested the residue of these decanted and evaporated solvents (quinine, beberine, strychnine), and examined the aqueous solution of the material, or one of the filtered alkaline liquids, in the usual way for acidulous radicals (citric, tartaric sulphuric, hypophosphorous). Or he has modified his methods to include search for some "scale preparation" which his special knowledge tells him has been newly introduced to, or is rare in, pharmacy.

In the case of liquids, the solvents as well as the dissolved matters claim attention. A few drops are evaporated to dryness on platinum foil to ascertain if solid matter of any kind is present; the liquid is tested by red and blue litmus-paper to ascertain if free alkalies, free acids, or neither are present; a few drops are heated in a test-tube and the odour of any vapour noticed, a piece of glass tubing bent to a right angle being, if necessary, adapted to the test-tube by a cork, and some of the distilled liquid collected and examined; finally, the usual group-reagents for the several basylous and acidulous radicals are consecutively applied.

Proceeding in this way, the student who has already had some experience in pharmacy, will not be likely to overlook such solvents as water, acids, alkalies, alcohol, glycerine, ether, chloroform, benzone, fixed oils, and essential oils, or to miss the substances which these menstrua may hold in solution. He will probably also recognise such liquids as carbolic acid, formic acid, lactic acid, methylic alcohol, aldehyde, aniline, nitrobenzene. He must not, however, suppose that he will always be able to qualitatively analyse, say, a bottle of medicine; for the various infusions, decoctions, tinctures, wines, syrups, liniments, confections, extracts, pill-masses, and powders contain vegetable matters most of which at present are quite beyond the reach of the analyst. Neither the highest skill in analysis nor the largest amount of experience concerning the odour, appearance, taste, and uses of drugs is sufficient for the detection of all these vegetable matters. Skill and experience combined, however, will do much; and in most cases even so difficult a task as the one just mentioned may be accomplished with reasonable success. Obviously, qualitative analysis alone will not enable the operator to produce a mixture of substances similar to that analysed; to this end recourse must be had to quantitative analysis, a subject treated subsequently.

Natural fluids, as "Milk" and "Urine" (*vide* Index), admit of special analytical treatment.

Gas-analysis, or *Eudiometry* (from εὐδία, *eudia*, calm air, and μέτρον, *metron*, a measure, in allusion to the *eudiometer*, an instrument used in measuring the proportion and, as the early chemists thought, the salubrity of the gases of the air) is a branch of experimental investigation, chiefly of a quantitative character, concerning which information must be sought in other treatises. The analysis of atmospheric air from various localities, coal-gas, and gases obtained in chemical researches, involves operations which are scarcely within the sphere of Chemistry applied to Medicine. Beyond the recognition, therefore, of oxygen, hydrogen, nitrogen, chlorine, carbonic, sulphurous, nitrous, and hydrosulphuric acid gases, etc., the experimental considerations of the chemistry of gaseous bodies may be omitted. Their study, however, should not be neglected, as existing conceptions of the constitution of chemical substances are largely dependent on the observed relations of the volumes of gaseous compounds to their elements. *See* previous paragraphs, pp. 8 to 22, 37 to 42, 51 to 55, and 144. A useful work on the latter part of the subject is a small book by Hofmann, "Introduction to Modern Chemistry."

Spectrum Analysis.—It may be well to state here that the preliminary and final examinations of minute quantities of solid matter may, in certain cases, profitably include their exposure to a temperature at which they emit light, the flame being physically analysed by a spectroscope. A spectroscope consists essentially of a prism to decompose a ray of light into its constituent colours, with tubes and lenses to collect and transmit the ray or rays to the eye of an observer. The material to be examined is placed on the end of a platinum wire, which is then brought within the edge of a spirit-lamp or other smokeless flame; volatilization, attended usually in the case of a compound by decomposition, at once occurs, and the whole flame is tinged with a characteristic hue. A flat ribbon of rays is next cut off by bringing near to the flame a brass tube, the cap of which is pierced by a narrow slit. At the other end of the tube, at focal distance for parallel rays, is a lens, through which the ribbon of light passes to a prism; the prism decomposes the ribbon, spreading out its constituent colours like a partially opened fan, and the coloured beam or *spectrum* thus produced is then examined by help of a telescope attached by a movable joint to a stand which carries the prism and the object-tube. It is this combination of tubes, lenses, and prism or prisms, which constitutes the spectroscope. Sodium compounds, under the circumstances, give yellow light only, indicated by a double band of light in a position corresponding to a portion of the yellow part of an ordinary solar spectrum. The potassium spectrum is mainly composed of a red and violet band; lithium a crimson, and, at very high temperatures, a blue band. Most of the other elements give equally characteristic spectra.

By passing white light through a coloured substance an "absorption spectrum" will be produced which is often characteristic, as in the case of blood or chlorophyll; while by aid of a combined microscope and spectroscope (microspectroscope) drops of coloured fluids can be analysed.

CHEMICAL TOXICOLOGY.

In cases of criminal and accidental poisoning, the substances presented to the chemical analyst for examination are usually articles of food, medicines, or vomited matters; or the liver, kidneys, intestines, stomach and contents, removed in course of post-mortem examination. In these cases some special operations are necessary before the poison can be isolated in a state of sufficient purity for the application of the usual tests; for in most instances the large quantity of animal and vegetable, or, in one word, organic matter present, prevents or masks the characteristic reactions on which the tests are founded. These operations will now be described*; they form the chemical part of the subject of Toxicology (τοξικὸν, *toxicon*, poison, and λόγος, *logos*, discourse).

Substances occurring apparently as definite salts or unmixed with organic matter need no special treatment. They are analysed by the ordinary methods already given, attention being restricted to poisonous compounds.

EXAMINATION OF AN ORGANIC MIXTURE SUSPECTED TO CONTAIN:—MERCURY, ARSENIUM, ANTIMONY, LEAD, COPPER, OR ZINC; SULPHURIC, NITRIC, HYDROCHLORIC, OXALIC, OR HYDROCYANIC ACIDS; CAUSTIC ALKALIES; PHOSPHORUS; STRYCHNINE, MORPHINE, OR OTHER POISONOUS ALKALOIDS.

Preliminary Examination.

Odour, Appearance, Taste.—Smell the mixture, with the view of ascertaining the presence or absence of any notable quantity of free hydrocyanic acid. Look carefully for any small solid particles, such as arsenic, corrosive sublimate, or verdigris, and for any appearance which may be regarded as abnormal, any character unusual to the coffee, tea, beer, medicine, vomit, coats of stomach, kidney, liver, or other organ, tissue, or solid matter under examination.

Poisonous Quantity of Acid.—Add to a small portion some solution of carbonate of sodium, with the view of ascertaining by strong effervescence the presence of any large, poisonous quantity of sulphuric, nitric, or hydrochloric acid (p. 673).

Poisonous Quantity of Alkali.—If so excessively alkaline as to require the addition of a very large quantity of acid before neutralization is effected, a noxious quantity of a corrosive or caustic alkali is present. Whether soda or potash, etc., is ascertained by the usual tests.

Special Instructions may induce the operator to suspect the presence of one particular poison. Direct examination for the latter may then be made, either at once, if the substance has an aqueous character, or when filtration or treatment with warm hydrochloric or acetic acid has afforded a more or less colourless liquid.

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* Materials for these experiments are readily obtained for educational purposes by dissolving the poison in infusions of tea or coffee, in porter or in water to which some mucilage of starch or linseed meal, pieces of bread, potato, and fat have been added.

Fluids.—A vomit or the contents of a stomach, if set aside in a long narrow vessel (test-glass or ale-glass), or, better, exposed on a filter during a night, will often yield a more or less limpid portion at the bottom or top of the solid matter. This fluid (separated by a pipette or otherwise) will sometimes respond to tests without further preparation, and always requires less preparatory treatment than a semi-solid mixture. If none passes through a filter, a portion often collects in the upper part.

General Procedure.—If the preliminary examination does not indicate the method to be pursued, proceed as follows, treating a portion (not more than one-fourth) of the mixture for the poisonous metals, another for the acids, and a third for alkaloids, reserving the remainder for any special experiments which may suggest themselves.

Examination for Mercury, Arsenium, Antimony, Lead, Copper, Zinc.

If a liquid, acidulate with hydrochloric acid and boil for a short time. If solid or semi-solid, cut up the matter into small pieces, add enough water to form a fluid mixture, stir in ten or twenty per cent. of ordinary liquid hydrochloric acid, and boil until, from partial aggregation and solution of the solid matter, filtration can easily be effected.

Heat a portion of the clear liquid with a thin piece of bright pure copper or copper gauze, about an inch long and a quarter of an inch broad, for about ten or twenty minutes; metallic *mercury*, *arsenium*, or *antimony* will be deposited on the copper, darkening it considerably in colour. Pour off the liquid from the copper, carefully rinse the latter with a little cold water, dry the piece of metal by holding it over or near a flame (using fingers, not tongs, or it may become sufficiently hot for loss of mercury or arsenium to occur by volatilization), introduce it into a narrow test-tube or piece of glass tubing closed at one end, and heat the bottom of the tube in a flame, holding it horizontally, that the upper part of the tube may be kept cool, and partially closing the mouth with the finger to prevent escape of vapour. Under these circumstances any *mercury* will volatilize from the copper and condense on the cool part of the tube in a ring or patch of white sublimate, readily aggregating into visible globules on being pressed by the side of a thin glass rod inserted into the tube; *arsenium* will volatilize from the copper, and, absorbing oxygen from the air in the tube, condense on the cool part of the glass in a ring or patch of white sublimate of arsenic (grey or even darker if much arsenium as well as arsenic be present), not running into globules when rubbed, but occurring in small crystals, the characteristic octahedral form of which (*vide* p. 193) is readily seen by aid of a good hand-lens, or the low power of a microscope; *antimony* volatilizes from the copper if strongly heated, and, absorbing oxygen, immediately condenses as a slight white deposit close to the metal.

Confirmatory Tests.—1. Nothing short of the production of globules should be accepted as evidence of the presence of mercury. It will usually have existed as corrosive sublimate. 2. To confirm indications of the presence of arsenium, a portion of the acid liquid may be subjected to the hydrogen tests (pp. 195–197); or the tube containing the white crystalline arsenic may be broken, and the part on which the sublimate occurs boiled for some time in water, and the hydrosulphuric-acid, ammonio-nitrate-of-silver, and ammonio-sulphate-of-copper tests (pp. 198, 200,) applied to the aqueous solution. 3. For antimony, a portion of the acid liquid must always be introduced into the hydrogen-apparatus with the usual precautions. (*Vide* p. 209.) 4. Any sulphur present may darken the copper, and such stained copper may subsequently yield a whitish sublimate of sulphur on the sides of the subliming tube; such appearances, therefore, are consistent with the entire absence of mercury, arsenium and antimony.

Note.—Before finally concluding that arsenium is absent from a fluid, the latter should be warmed with a little sulphurous acid, and ordinary tests then again applied; for arsenic acid and other arseniates are not readily affected by the usual reagents for arsenium.

For *lead* and *copper*, pass hydrosulphuric acid through the clear acidulated liquid for some time, warming the liquid if no precipitate is produced, or diluting and partially neutralizing the acid by ammonia if much acid has been added. Collect on a filter any black precipitate that may have formed; wash, dissolve in a few drops of aqua regia, dilute, and apply tests, such as ammonia for copper, sulphuric acid for lead, or any other of the ordinary reagents (pp. 219, 246).

Copper may often be at once detected in a small quantity of acidulated liquid by immersing the point of a penknife or a piece of bright iron wire—a deposit of copper, in its characteristic colour, quickly or slowly appearing, according to the amount present (p. 219).

Zinc.—To the acid liquid through which sulphuretted hydrogen has been passed, add excess of ammonia (or to the original acid fluid add excess of ammonia, and then sulphydrate of ammonium); a precipitate falls which may contain alumina, phosphates, and zinc. (It is usually blackish, from the presence of sulphide of iron.) Collect the precipitate on a filter, wash, dissolve in a little hydrochloric acid, add a few drops of nitric acid, boil, pour in excess of ammonia, filter, and test the filtrate with sulphydrate of ammonium; a white precipitate indicates zinc.

Examination for Mineral Acids, Oxalic and Hydrocyanic Acids.

To detect *hydrochloric*, *nitric*, or *sulphuric acid* in a liquid containing organic matter, dilute with water and apply to small portions the usual tests for each acid, disregarding indications of small quantities. (*Vide* pp. 311, 336, 364.)

Excessive sourness, copious evolution of carbonic acid gas on the addition of carbonate of sodium, and abundant evidence of acid on applying the various tests to small portions of the fluid presented for analysis, collectively form sufficient evidence of the occurrence of a poisonous amount of either of the three common mineral acids. Small quantities of the hydrochloric, nitric, and sulphuric radicals, occurring as metallic salts or acids, are common normal constituents of food; hence the direction to disregard insignificant indications. If the fluid under examination be a vomit or the contents of a stomach, and an antidote has been administered, free acid will not be found, but, instead, a large amount of the corresponding salt.

For *oxalic acid*, filter or strain a portion of the liquid, if not already clear, and add solution of acetate of lead so long as a precipitate occurs; collect the precipitate, which in any case is only partly oxalate of lead, on a filter, wash, transfer it to a test-tube or test-glass, add a little water, and pass hydrosulphuric acid through the mixture for a short time; the lead is thus converted into the insoluble form of sulphide, while any oxalic acid is set free in the solution. Filter, boil to get rid of hydrosulphuric acid, and apply the usual tests for oxalic acid (*see* p. 372) to the clear filtrate.

The contents of a stomach containing oxalic acid will often be of a dark-brown colour with a tinge of green (altered blood and mucus), and the viscid mixture generally, though slowly, affords some clear, limpid, almost colourless, liquid by filtration or on standing.

For *hydrocyanic acid*, the three chief tests may be applied at once to the liquid or semi-liquid organic mixture, whether it has an odour of hydrocyanic acid or not. First:—Half fill a small porcelain crucible with the material, add eight or ten drops of strong sulphuric acid, stir gently with a glass rod, and invert over the mouth of the crucible a watch-glass moistened with a small drop of solution of nitrate of silver;

a white film on the silver solution is probably cyanide of silver, formed by the action of the gaseous hydrocyanic acid on the nitrate of silver. Second :—Prepare a small quantity of the organic mixture as before, slightly moistening the centre of the watch-glass with solution of potash; here, again, the heat generated by the action of the strong acid is sufficient to volatilize some of the hydrocyanic acid, which, reacting on the potash, forms cyanide of potassium. On removing the watch-glass and stirring into it successively solution of a ferrous salt, a ferric salt, and hydrochloric acid, flocks of Prussian blue are produced if hydrocyanic acid is present. Third :—Proceed as before, moistening the watch-glass with sulphydrate of ammonium; after exposure to the hydrocyanic acid gas for five or ten minutes, add a drop of solution of ammonia, evaporate to dryness at a low temperature, and add a drop of hydrochloric acid and of solution of perchloride of iron; a blood-red colour, due to sulphocyanate of iron, is produced if cyanogen is present.

If the above reactions are not well marked, the organic mixture may be carefully and slowly distilled in a small retort, the neck of which passes into a bottle and dips beneath the surface of a little water at the bottom of the bottle; the reagents may then be applied to separate portions of the distillate.

The examination of organic mixtures for hydrocyanic acid must be made without delay, as the poison soon begins to decompose, and in a day or two is usually destroyed.

Examination for Phosphorus.

A paste containing phosphorus is commonly employed for destroying vermin. In cases of poisoning, the phosphorus is generally in sufficient quantity to be recognised by its characteristic unpleasant smell. A stomach in which it occurs not infrequently exhibits slight luminosity if opened in a dark room. When the phosphorus is too small in quantity or too much diffused to afford this appearancc, a portion of the material is placed in a flask, water acidulated by sulphuric acid added, a long wide glass tube fitted to the neck of the flask by a cork, and the mixture gently boiled. If phosphorus is present (even 1 part in 2,000,000, according to De Vrij) the top of the column of steam as it condenses in the tube will appear distinctly phosphorescent when viewed in a dark room. From its liability to oxidation, phosphorus cannot be detected after much exposure of an organic mixture to air.

Examination for Strychnine and Morphine.

Strychnine.—If solid or semi-solid, digest the matter with water and about ten per cent. of hydrochloric acid till fluid, filter, evaporate to dryness over a water-bath. If the organic mixture is already liquid, it is simply acidulated with hydrochloric acid and evaporated to dryness. The acid residue is next treated with spirit of wine as long as anything is dissolved, the filtered tincture evaporated to dryness over the water-bath, and the residue digested in water and filtered. This slightly acid aqueous solution must now be rendered alkaline by ammonia, and well shaken in a closed bottle or long tube with about half an ounce of chloroform, and set by till the chloroform has subsided. The chloroform (which contains the strychnine) is then removed by a pipette, the presence of any aqueous liquid being carefully avoided, and evaporated to dryness in a small basin over a water bath, the residue moistened with concentrated sulphuric acid, and the basin kept over the water-bath for several hours. (It is highly important that the sulphuric acid used in this operation should be free from nitrous compounds. Test the acid, therefore, by adding powdered sulphate of iron, which becomes pink if nitrous bodies are present. If these are found, the acid should be purified by strongly heating with sulphate of ammonium, seventy or eighty grains to a pint.) The charred material is exhausted with water, filtered, excess of ammonia added, the filtrate shaken with about a quarter of an ounce of chloroform, the mixture set aside for the chloroform to separate, and the chloroform again removed. If on evaporating a small portion of this chloroform solution to dryness, adding a drop of sulphuric acid to the residue, and warming, any darkening of colour or charring takes place, the strychnine is not sufficiently pure for chemical detection; in that case the rest of the chloroform must be removed by evaporation, and the residue redigested in warm sulphuric acid for two or three hours. Dilution, neutralization of acid by ammonia, and agitation with chloroform is again practised, and the residue of a small portion of the chloroform solution once more tested with sulphuric acid. If charring still occurs, the treatment must be repeated a third time. Finally a part of the chloroform solution is taken up by a pipette and drop after drop evaporated on one spot of a porcelain crucible-lid until a fairly distinct dry residue is obtained. A drop of sulphuric acid is placed on the spot, another drop placed near, a minute fragment of red chromate of potassium placed in the second drop, and, when the acid has become tinged with the chromate, one drop drawn across the other; the characteristic evanescent purple colour is then seen, if strychnine is present. Other tests (*vide* p. 630) may be applied to similar spots.

This is Girdwood and Rogers's method for the detection of strychnine when mixed with organic matter. It is tedious but trustworthy, and, though apparently complicated, very simple in principle, thus—strychnine is soluble in acidulated water or alcohol, or in chloroform, readily removed from an alkaline liquid by agitation with chloroform, and not charred or otherwise attacked when heated to 212° F. with sulphuric acid: much of the organic matter of the food is insoluble in water; of that soluble in water, much is insoluble in alcohol; and of that soluble in both menstrua, all is charred and destroyed by warm sulphuric acid in a shorter or longer time. (*See* also Stas's general process, p. 679.)

Morphine and the Meconic Acid with which it is associated in Opium.—To the liquid or the semi-fluid mixture, warmed for some time with a small quantity of acetic acid, filtered, and concentrated if necessary, add solution of acetate of lead until no further precipitate is produced. Filter and examine the *precipitate* for meconic acid, reserving the *filtrate* for the detection of morphine.

The Precipitate.—Wash the *precipitate* (meconate of lead, etc.) with water, place it in a test-tube or test-glass with a small quantity of water, pass hydrosulphuric acid gas through the mixture for a short time, filter, slightly warm in a small basin, well stirring to promote removal of excess of the gas, and add a drop of neutral solution of perchloride of iron; a red colour, due to the formation of meconate of iron, is produced if meconic acid is present. This colour is not destroyed on boiling the liquid after the addition of one drop of diluted hydrochloric acid, as is the case with ferric acetate, nor is it bleached by solution of corrosive sublimate, thus distinguishing it from ferric sulphocyanate. It is discharged by hydrochloric acid.

The Filtrate.—The solution from which meconic acid has been removed by acetate of lead is evaporated to a small bulk over a water-bath, excess of carbonate of potassium added, and evaporation continued to dryness. The residue is then treated with alcohol, which dissolves the morphine. The alcoholic solution evaporated similarly may leave the morphine sufficiently pure for the application of the usual tests (*vide* p. 619) to small portions of the residue. If no reaction is obtained, add a drop of sulphuric acid and a little water to the residue, and shake with ether, in which the salt of morphine is insoluble. The treatment with ether may be repeated until nothing more is removed, the acid aqueous liquid saturated with carbonate of potassium, the mixture evaporated to dryness, the residue digested in alcohol, filtered, and portions of the alcoholic liquid evaporated to obtain spots of morphine for the application of the ordinary tests.

If much organic matter is believed to remain in the filtrate after the acetate of lead treatment, or if a considerable excess of acetate of lead has been employed, the filtered liquid should be subjected to a current of sulphuretted hydrogen until no more sulphide of lead is precipitated, the mixture filtered, and the filtrate, with the washings from the sulphide of lead, evaporated to a small bulk, excess of carbonate of potassium added, the whole well mixed and agitated with twice or thrice its bulk of a mixture of ether and acetic ether (ether alone might not dissolve the morphine). On standing, the ethereal liquid rises to the surface: it is carefully removed, evaporated to dryness, and the residue tested or further purified in the manner described in the preceding paragraph.

The examination for morphine must be conducted with great care, and with as large a quantity of material as can be spared; for its isolation from other organic matter is an operation of difficulty, especially when only a minute proportion of alkaloid is present. Fortunately the detection of meconic acid does not include similar difficulties; and as its reactions are quite characteristic, its presence is held to be strong evidence of the existence of opium in an organic mixture.

Examination for other Poisonous Alkaloids.

Stas's Process.—Minutely subdivide any solid matter; to this and the liquid portion of the vomit, etc., add about twice their weight of the strongest spirit of wine containing sufficient tartaric acid to fairly acidify the mixture. Digest the whole in a flask at a temperature of 150° or 160° F.; set aside to cool; filter. The solution, which will contain the whole of the alkaloid, should then be evaporated nearly to dryness *in vacuo*, or at all events at a temperature not exceeding 100° F., lest volatile alkaloids should be dissipated. The residue is next exhausted with cold anhydrous alcohol; filtered; and the filtrate evaporated to dryness with the precautions already stated. The extract is dissolved in a very small quantity of water, treated with excess of powdered bicarbonate of sodium or potassium, and well shaken with five or six times its volume of pure ether (with perhaps a little acetic ether). This ethereal liquid contains the alkaloid. Small portions should be evaporated in watch-glasses and tasted, or tested physically and chemically, according as the knowledge of collateral circumstances by the operator, or his experience, or such reactions as are recorded on pp. 632-648 may suggest.

If a volatile alkaloid (conine, nicotine, lobeline, sparteine) is indicated, the ethereal solution, which may contain animal matter, is removed, agitated with aqueous solution of potash, decanted, and shaken with pure diluted sulphuric acid. On standing, the aqueous portion, containing the alkaloid as acid sulphate, subsides; the upper ethereal portion containing the animal matter is rejected; the acid aqueous liquid is made alkaline with caustic potash or soda; ether added; well shaken; the ethereal liquid decanted, evaporated to dryness *in vacuo*, or at a low temperature, and (to get rid of all traces of ammonia) again moistened with ether and dried. The residue is now tested for the suspected alkaloid by taste, smell, and the application of appropriate reagents (pp. 632–648).

If a non-volatile alkaloid (aconitine, atropine, brucine, colchicine, emetine, hyoscyamine, physostigmine, solanine, veratrine, as well as morphine, codeine, and strychnine, etc). is indicated, further purifiy by decanting the ethereal liquid from the lower aqueous solution of bicarbonate of sodium, removing the ether by evaporation, digesting the residue in alcohol, filtering, evaporating the alcohol, treating the residue with diluted sulphuric acid, setting aside for a few hours, filtering, concentrating, adding powdered carbonate of potassium, and finally anhydrous alcohol. The alcoholic liquid, on evaporation, yields the alkaloid in a fit condition for testing in the manner already stated.

Sonnenschein's Process.—Digest with diluted hydrochloric acid, evaporate to the consistence of syrup, dilute, set aside for some hours, filter. Add solution of phosphomolybdic acid so long as any precipitate falls or cloudiness occurs; collect the precipitate on a small filter; wash it with water containing phosphomolybdic and nitric acid, and, while still moist, place it in a flask. Decompose this compound of phosphomolybdic acid and alkaloid by adding caustic baryta until the stirred mixture is distinctly alkaline. Distil off volatile alkaloids, condensing and collecting by help of a long tube so bent that the apparatus shall act as a retort, the end of the tube being attached to a bulb or a series of bulbs containing diluted hydrochloric acid. The acid liquid evaporated gives a residue of hydrochlorates of alkaloids. The latter will afford characteristic reactions with the tests for the suspected alkaloid, and, on being moistened with baryta-water and warmed, will afford fumes of volatile alkaloids the odour of which is usually characteristic. The residue in the flask will contain non-volatile alkaloids. It is treated with carbonic acid gas to neutralize and precipitate the excess of baryta as insoluble carbonate of barium; the mixture is evaporated to dryness over a water-bath; and the residue digested in alcohol. The alcoholic solution evaporated generally yields the alkaloids in a fit state for testing.

Reagents for Alkaloids.

Phosphomolybdic acid forms with ammonia, in acid solutions, a remarkably insoluble compound; and it comports itself in a similar manner with those compounds which are analogous to ammonia—the nitrogenized organic bases—consequently forming an excellent reagent for their detection. It may be prepared in the following manner: Molybdate of ammonium is precipitated by phosphate of sodium; the yellow precipitate, having been washed, is diffused through water, and heated with sufficient carbonate of sodium to dissolve it. The solution is then evaporated to dryness, and calcined to drive off the ammonia. In case any of the molybdic compound be reduced by this operation, the residue must be moistened with nitric acid and again calcined. The dry mass is then dissolved in cold water, the solution strongly acidulated with nitric acid, and water added until ten parts of the solution contain one of the dry salt. The liquid, which is of a golden-yellow colour, must be preserved from ammoniacal fumes. It precipitates all the alkaloids (with the exception of urea) when a mere trace only is present. The precipitates are yellow, generally flocculent, insoluble in water, alcohol, ether, and the diluted mineral acids, with the exception of phosphoric acid. Nitric, acetic, and oxalic acids, concentrated and boiling, dissolve them. Those compounds are decomposed by the alkalies, certain metallic oxides, and the alkaline salts, which separate the alkaloid. To give an idea of the sensitiveness of this reagent, it may be stated that 0·000071 gramme of strychnine gives an appreciable precipitate with one cubic centimetre of the solution of phosphomolybdic acid.

Phosphoantimonic and phosphotungstic acids are also precipitants of alkaloids. The chlorides of platinum, iridium, palladium, and gold are occasionally serviceable. Tannic and picric acids, too, may be used, and a solution of iodine and iodide of potassium.

Other special reagents for alkaloids are "Mayer's"; "Nessler's" (*see* Index); the double iodide of potassium and cadmium; and a solution of the double "Iodide of Bismuth and Potassium." The latter is made (by Thresh) by adding together one ounce of *Liquor Bismuthi*, B.P., 90 grains of iodide of potassium, and 90 grains of strong hydrochloric acid. This orange-coloured solution gives a red precipitate with dilute cold solutions containing alkaloids.

Ptomaines (πτῶμα, a corpse) have already been alluded to as including poisonous alkaloids producible from putrefying animal matters, even the human body itself, during the ordinary processes of decay. They are distinguished, according to Brouardel and Boutmy, by a drop or two of a solution of their sulphate converting a drop of solution of ferricyanide of potassium into ferrocyanide, the mixture then giving a dark-blue precipitate with a ferric salt. Some other substances also, as morphine, possess this converting power.

Tyrotoxicon.—This ptomaine (p. 561) may be isolated and tested as follows: Prepare an aqueous extract of the cheese, or filter the coagulated milk, etc. No heat should be applied, and undue exposure to air should be avoided by using stoppered bottles. Make the filtered fluid faintly alkaline with carbonate of sodium, and well shake with half its bulk of ether. Allow the perfectly clear othereal solution to evaporate spontaneously; and, if necessary, again extract this aqueous residue with water, shaking with ether and evaporating as before. The resulting residue may be tested in two or three ways. A little placed on the tongue and swallowed will cause more or less of nausea, vomiting, purging, and headache. Again, the residue is either characteristically crystalline, or will become so after standing in a vacuum over sulphuric acid. Mix two or three drops of sulphuric acid and carbolic acid on a white plate, and add a few drops of the aqueous residue just mentioned; if an orange-red or purple colour results, the presence of tyrotoxicon may be suspected, but any nitrate or nitrite present may cause a similar colour. To some of the aqueous residue add an equal volume of a saturated solution of caustic potash; the double hydrate of potassium and diazobenzene is then formed and appears in six-sided plates, whereas any nitrate of potassium appears in prisms. This residue may be treated with absolute alcohol, filtered, and the filtrate evaporated, when the plates may again be observed or the colour reaction again obtained with this purified product (Vaughan).

Obscure Poisons.—Many substances, the active principles of which are at present beyond the reach of the chemical analyst, are poisons of a more or less active character. (*See* the *Pharmaceutical Journal* for Sept. 6, 1879, p. 195, and for Dec. 20, 1879, p. 481.)

"Chloral Hydrate," p. 579, and "Chloroform," p. 476, are now included in "Part 2 of Schedule A" as "poisons within the meaning of the Pharmacy Act, 1868." "Cantharides" is in "Part 1." Its active principle is isolated as described on page 503, and is recognised by its blistering action on any thin spot on one's skin.

ANTIDOTES.—*Vide* "Antidotes" in the Index.

QUESTIONS AND EXERCISES.

In examining food and similar matter for poison, why must not the ordinary tests for the poison be at once applied?—What preliminary operations should be performed on a vomit in a case of suspected poisoning?—How would you search for corrosive sublimate in wine?—By what series of operations would you satisfy yourself of the presence or absence of arsenic in the contents of the stomach?—Describe the treatment to which decoction of coffee should be subjected in testing it for tartar-emetic.—State how the occurrence of lead in water is demonstrated.—Give a process for the detection of copper in jam.—How would you detect zinc in a vomit?—How may the presence of much sulphuric acid in gin be proved?—In testing ale for nitric acid, what reactions would you select?—Show how you would conclude that a dangerous quantity of hydrochloric acid had been added to cider.—Describe the manipulations necessary in testing for hydrocyanic acid in the contents of a stomach.—By what method is oxalic acid discovered in infusion of coffee?—How is phosphorus detected in organic mixtures?—Give the process by which strychnine is isolated from a vomit.—Mention the experiments by which the presence of laudanum in porter is demonstrated.—Name the anti dotes in cases of poisoning by:—*a*, alkaloids; *b*, antimonials; *c*, arsenic *d*, barium salts; *e*, copper compounds; *f*, hydrochloric acid; *g*, hydrocyanic acid; *h*, salts of lead; *i*, corrosive sublimate; *j*, nitric acid; *k*, oxalic acid; *l*, salts of silver; *m*, oil of vitriol; *n*, tin liquors; *o*, zinc salts; *p*, carbolic acid.

EXAMINATION OF MORBID URINE AND CALCULI.

The various products of the natural and continuous decay of animal tissue and the refuse matter of food are eliminated from the system chiefly as fæces, urine, and expired air. Air exhaled from the lungs carries off from the blood much carbon (about 8 ozs. in 24 hours) in the form of carbonic acid gas, and some aqueous vapour—the latter, together with a small amount of oily matter, also escaping by the skin. Directing the breath to a cold surface renders moisture evident; and breathing through a tube into lime-water demonstrates the presence of a considerable quantity of carbonic acid gas. The fæces consist mainly of the insoluble *débris* of the system, the soluble matters and water forming the urine. These excretions vary considerably, according to the food and general habits of the individual and external temperature But in disease the variations become excessive; hence their detection by the medical practitioner, or by the pharmacist for the medical man, is a matter of importance.

An analysis of fæces or air cannot be made with sufficient ease and rapidity to be practically available in medical diagnosis. But with regard to urine, certain abnormal substances and abnormal quantities of normal constituents may be chemically detected in the course of a few minutes by any one having already some knowledge of chemical manipulation.

Healthy human urine contains in 1,000 parts, 957 of water, 14 of urea, 1 of uric acid, 15 of other organic matter, and 13 of inorganic salts. The amount passed in twenty-four hours varies from two to three pints in an adult, and its specific gravity, if healthy, will range from 1·015 to 1·025. Any considerable deviation from these limits would suggest a possibly pathological condition. The average amount of solid matter passed by the urine in one day is 1½ to 2 ounces.

Physical Examination of Urine.

Normal urine is either of a pale yellow colour or faintly reddish-yellow, due to a pigment termed *urobilin*. Urine has a reddish-brown tint if blood is present, or greenish-brown if bile is present. Both colour and odour are much influenced by certain kinds of food and by some drugs.

Fresh urine is clear. Any turbidity may be due to urates, phosphates, or pus. Urates redissolve when the urine is warmed; phosphates by the addition of acetic acid; pus is detected by the microscope, *vide infra.* If the urine be turbid from the presence of phosphates when first voided, it may be due to conversion of urea into carbonate of ammonium, which precipitates the phosphates within the bladder, in which case the fresh and warm urine will effervesce slightly on the addition of acetic acid. This condition is abnormal.

On standing, healthy urine commonly gives a slight cloud of mucus, and after severe exercise, or after a hearty nitrogenous meal, may give a sediment of urates.

The specific gravity of urine should be taken on a specimen removed from the whole bulk excreted in twenty or twenty-four hours. Many qualitative experiments and all quantitative operations should only be performed on the mixed urine of twenty-four hours.

Healthy urine when fresh is always slightly acid, the acidity being said to be due to the presence of acid phosphate of sodium. Alkalinity is probably due to that conversion of urea into carbonate of ammonium within the bladder already described.

EXAMINATION OF MORBID URINE FOR ALBUMEN, SUGAR, BILE, EXCESS OF UREA, OR DEFICIENCY OF CHLORIDES; AND URINARY SEDIMENT FOR URATES (OR LITHATES), PHOSPHATES, OXALATE OF CALCIUM, AND URIC ACID.

Albumen.—To detect albumen, acidulate a portion of the clear urine in a test-tube with a few drops of diluted nitric acid (to keep phosphates in solution), and boil; flocks or coagula will separate if albumen be present. To detect small quantities, nearly fill a long test-tube with clear urine (filtered, if necessary) and faintly acidulated with acetic acid; then, holding the tube by its lower end, boil the upper portion of the urine.——A cloudiness in the boiled portion, which, on addition of a few drops of acetic acid, does not disappear, indicates the presence of albumen.——Or, heat a little nitric acid in a test-tube, and carefully pour down the side a little of the urine, so as to overlie the acid. If albumen be present, a whitish ring or coagulum will, sooner or later, be formed at the junction of the fluids.

These experiments should first be made on normal urine containing a drop or two of solution of white of egg. The coagulum is white if it is only albumen, greenish if bile-pigment be present, and brownish-red if the urine contain blood. The influence of acids and alkalies on the precipitation of albumen is noticed on page 650.

A saturated solution of picric acid at once precipitates any albumen from urine. Should the urine be alkaline, it must be acidified before applying this test. On warming the mixture, the precipitate will become more pronounced if due to the albumen or globulin of blood, or to any modifications of albumen caused by acidity or alkalinity of urine; but will disappear if due to peptone or propeptone. Ferrocyanide of potassium, also, will precipitate the former varieties of albumen, but not the peptones.

The occurrence of albumen in the urine may be temporary and of but little importance; or it may indicate the existence of a serious affection, known as Bright's disease. "Albumenuria is rarely a serious condition unless it is sufficiently pronounced to be made out by the cold nitric acid test" (Steward).

For quantitative purposes, Esbach employs the picric test, dissolving 10 parts of picric acid and 20 of citric acid in 900 of water, by aid of heat, and when the solution is cold, diluting with water to 1,000 parts. This solution is added to a given volume of urine in a graduated Cetti's Esbach tube, and the height of the precipitate is noted after 24 hours. Johnson finds a simple solution of 5 grains of picric acid in 1 fluid ounce of water better than Esbach's solution, because the excess of acid in the latter tends to precipitate much uric acid which would be reckoned as albumen. A standard value is given to the solution in the first instance by washing, drying and weighing the albumen.

Sugar.—To a portion of the clear urine in a test-tube add five or ten drops of solution of sulphate of copper; pour in solution of potash or soda until the precipitate first formed is re-dissolved; slowly heat the solution to near the boiling-point; a yellow, yellowish-red, or red precipitate (cuprous oxide) is formed if sugar be present. (The production of a rose-red or pink tint with the cold alkaline copper solution indicates the presence of the altered non-coagulable albumenoids termed *peptones*).

This experiment should be first made on urine containing a drop or two of solution of grape-sugar (p. 557). The hydrate of copper precipitated by the alkali is insoluble in excess of pure potash or soda, but readily dissolves if organic matter, especially sugar, be present. The copper salt should not contain iron.

Other tests may be applied if necessary (*vide* p. 561). *See* also "Sugar, Quantitative Estimation of," in Index.

A minute amount of sugar is said to occur in normal urine, and a distinct trace is occasionally present. In searching for small quantities, uric acid, which also reduces the copper-solution, should first be removed. (*See* p. 427.) Normal urine rotates a ray of plane polarized light slightly to the left, but if even a small amount of sugar be present, marked dextro-rotation results. In larger quantities (often 5 per cent.) sugar is a characteristic constitutent of the urine of diabetic patients, greatly increasing the specific gravity of the secretion. Small hydrometers (termed *urinometers*) are commonly employed for quickly and readily ascertaining the specific gravity of urine; they range from 1·000 to 1·050, the interval of 1·015 to 1·025 being marked as "H.S." or "healthy state." (*Vide* "Specific Gravity" and "Hydrometers" in Index; also "Sugar, Quantitative Estimation of.")

Bile.—This is detected by the dark greenish-brown colour of the urine and by the general test (Pettonkofer's, or still better, Quinlan's) described on page 658. Or a little of the urine may be placed on a white plate, and strong nitric acid, containing some nitrous acid, dropped on it; a peculiar play of colours—green, yellow violet, etc.—occurs if (the colouring-matter of) bile be present (Gmolin). In doubtful cases the urine should be thoroughly shaken up with a little chloroform, which dissolves the bile-pigments, and the acid test applied to the separated chloroform. Oliver recommends that the urine be diluted to a sp. gr. of 1·008 and then one volume be added to three volumes of the following reagent, when more or less opalescence will be produced, according to the amount of bile acids present. For the reagent, dissolve 30 grains of flesh peptone, 4 grains of salicylic acid, and 33 minims of official acetic acid, in 8 ounces of water; filter.

Excess of Uric Acid.—A rough quantitative process consists in applying the qualitative method already described (p. 427) to a known volume of urine, and collecting on a filter, washing and weighing the resulting uric acid. The result is always low. Hopkins *saturates* the urine with chloride of ammonium, and, after a couple of hours, decomposes the separated urate of ammonium by hydrochloric acid, and collects, washes, dries and weighs the resulting uric acid. Vide *Proceedings of the Royal Society*, vol. lii., p. 93.

Excess of Urea.—About one-third of the solid matter in the urine is urea. Its proportion varies considerably; but $1\frac{1}{2}$ per cent. may be regarded as an average amount. Concentrate urine slightly by evaporation in a small dish, pour the liquid into a test-tube, set the tube aside till cold, or cool it by letting cold water run over the outside, add an equal bulk of strong nitric acid, and again set aside; scaly crystals of nitrate of urea are deposited more or less quickly.

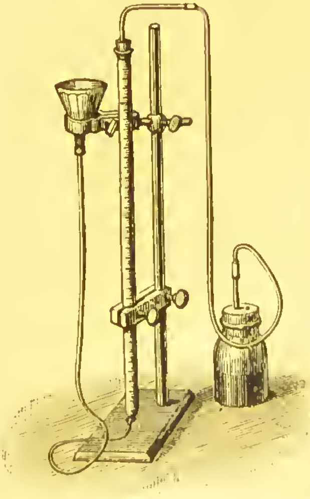
With regard to the amount of urea in urine, it is impossible to sharply define excess or deficiency. If nitric acid gives crystals without concentration, excess is certainly present in the sample examined: though, if the amount of urine passed in the twenty-four hours is much below the average, the quantity of urea excreted may not be abnormal. A rough estimate may be formed by mixing a few drops of the urine and acid on a piece of glass and setting aside; the time which elapses before crystals form is an indication of the quantity in the specimen. The time will vary according to the temperature and state of moisture of the atmosphere; but with care some useful comparative results may in this way be obtained.

For trustworthy quantitative estimations, the urine is shaken with an alkaline solution of recently prepared hypobromite of sodium, and the nitrogen then liberated, collected and measured. The reaction is of the following character:—

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\substack{\text{Hypobromite}\\ \text{of sodium.}}}{3NaBrO} = \underset{\substack{\text{Bromide}\\ \text{of sodium.}}}{3NaBr} + \underset{\substack{\text{Carbonic}\\ \text{acid gas.}}}{CO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2}$$

The whole of the nitrogen of the urea, however, is not evolved, while, on the other hand, some of the produced nitrogen is yielded by the uric acid, hippuric acid, and creatinine of the urine. Neither fact is of any consequence in this examination of urine, for a given specimen of urine always yields the same quantity of gas, hence a given volume of gas always indicates the same percentage of urea, and once a measuring-tube is so divided as to indicate percentages of urea when a given volume of urine is used, it may be trusted to indicate the varying percentages of urea in the urine of one patient, or the different proportions of urea in the urine of different patients. The method is Davy's with improvements and modifications of apparatus by Knop, Huefner, Russell and West, Apjohn, Dupré, Gerrard, Gillet, and others. In the chemical laboratory, appliances already at hand may be adapted for the operation. Thus, as shown in the adjoining woodcut, any two-ounce or three-ounce bottle serves for the reaction between the hypobromite and urine; a 50 or 60 c.c. burette, containing water, may be the measuring-tube; while a funnel, supported in the ring of a retort-stand, serves both as a reservoir for water displaced by the evolved nitrogen, and as a means of getting that equal level of water within and without the measuring-tube which shall prevent misleading attenuation or compression of the nitrogen. Attach the funnel to the bottom of the burette by india-rubber tubing. Attach a short glass tube by a pierced cork to the top of the burette, and, by more india-rubber tubing, connect this glass tube with a similar tube in the well-fitting india-rubber cork of the gas-generating bottle. Disconnect the latter. Into the funnel pour water until it rises to the zero mark of the burette and a little water remains in the bottom of the funnel. Into the generating-bottle pour about 25 c.c. of solution of soda (made by dissolving about 100 grammes of solid soda in 250 c.c. of water)

Fig. 50.



and about 2·5 c.c. of bromine. Into the bottle containing the hypobromite solution thus prepared, a short test-tube containing 5 c.c. of urine is lowered, care being taken that no urine is spilt. The cork is re-inserted and the water-level again adjusted (best accomplished if into the cork of the generating bottle be fitted a short glass tube, the external orifice of which can be closed by a cork or a cap as soon as the apparatus is ready for use). The generating-bottle is now inclined, when, the urine and hypobromite mixing, nitrogen is at once evolved (the carbonic acid produced at the same time being absorbed by the strongly alkaline fluid in the bottle). The funnel is lowered until the surfaces of the water inside and outside the measuring-tube are on a level; after ten or fifteen minutes the level is finally adjusted and the amount of produced gas noted. Every 55 c.c. of gas indicate 0·15 of a gramme of urea, the temperature being about 66° F. and the height of the barometer being about 30 inches. In cases in which frothing interferes, put a fragment of suet into the generating-bottle.

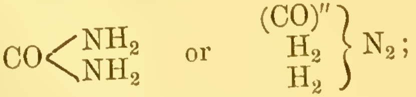
Instead of hypobromite of sodium, the hypochlorite, which is more stable, may be employed (Squibb).

Tests.—Urea in solution in water may be detected by the reaction with nitric acid, and by the readiness with which it yields ammonia on being boiled with alkalies. In putrid urine its conversion into an ammoniacal salt has already been effected by ammoniacal fermentation.

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carbonate of ammonium.}}{(NH_4)_2CO_3}.$$

This transformation of the urea into carbonate of ammonium is due to the action of a special ferment belonging to the genus Torula, formed of chaplets of globules similar in form to, but much smaller than, those of beer yeast. It occurs as a white deposit in the urine. If some of this deposit be added to a saccharine solution containing urea, it rapidly multiplies, carbonate of ammonium being formed.

Formula of Urea.—The empirical formula of urea is CH_4N_2O. Its rational formula may be thus written,—



$$CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} \quad \text{or} \quad \left.\begin{matrix}(CO)''\\ H_2\\ H_2\end{matrix}\right\} N_2;$$

that is it may be regarded as carbamide or as one of the organic bases already referred to, a primary diamine, in which the bivalent radical CO occupies the place of H_2. The other atoms of hydrogen may be displaced by various radicals, and many *compound ureas* thus be obtained.

Artificial Urea. — Urea may be prepared artificially by Williams's modification of Wöhler's method. Cyanide of potassium, of the best commercial quality (containing about 90 per cent. of real cyanide), is fused at a very low red heat in a shallow iron vessel; red lead is added in small quantities at a time, the temperature being kept down by constant stirring. When the red lead ceases to cause further action, the mixture (lead and cyanate of potassium) is allowed to cool, the product finely powdered, exhausted with cold water, nitrate of barium added till no more precipitate (carbonate of barium) falls, the mixture filtered, and the filtrate treated with nitrate of lead so long as cyanate of lead is thrown down. The latter is thoroughly washed, and dried at a low temperature. Equivalent quantities of cyanate of lead and sulphate of ammonium digested in a small quantity of water with a little heat (*vide* p. 400) and filtered, yield a solution from which urea crystallizes on cooling.

Another Process.—Basaroff has found that urea is produced when ordinary carbonate of ammonium is heated in *strong* hermetically sealed tubes to about 275° F. for a few hours. The same chemist had previously obtained urea by similarly heating pure carbamate of ammonium; so that the source of the urea in the former case is probably the carbamate of ammonium believed to occur in the carbonate (*see* p. 100).

$$NH_4NH_2CO_2 - H_2O = CO(NH_2)_2.$$

Deficiency of Chlorides.—Any given bulk of urine in a test-tube yields, of course, abundance of flocks of chloride of silver on the addition of nitric acid and nitrate of silver. Any markedly smaller bulk points to pathological conditions, such as those of acute fever.

Chromogens.—Urine may contain chromogens, which are substances which do not at the time colour the urine but which, on the addition of oxydizing reagents, or after standing some time, develop a colour. A blue colour may be seen in urine on the addition of much nitric acid. This is due to the formation of indigo from its chromogen. The darkening often noticed on the addition of acid to urine is due to liberation of the pigment urobilin from its chromogen.

Care must be taken not to confound the colour-changes in urine due to the action of drugs with the effects produced by the action of oxydizing agents on chromogens. Thus rhubarb and santonin darken the natural yellow of urine, the addition of an alkali causing a red coloration. Carbolic acid taken internally makes the urine greenish black, resembling urine with much bile in it. If iodide or bromide of potassium is being taken internally, the addition of a strong acid will often cause separation of iodine or bromine respectively in the urine.

URINARY SEDIMENTS.

Warm the sediment with the supernatant urine, and filter.

<table>
<tr><td colspan="3"><i>Insoluble.</i>
Phosphates, oxalate of calcium, and uric acid.
Warm with acetic acid, and filter.</td><td rowspan="3"><i>Soluble.</i>
Urates—of ammonium, calcium, or sodium; chiefly the latter.
They are redeposited as the liquid cools, and if sufficient in quantity may be further examined for ammonium, calcium, sodium, and the uric radical by the appriate tests.</td></tr>
<tr><td colspan="2"><i>Insoluble.</i>
Oxalate of calcium and uric acid.
Warm with hydrochloric acid, filter.</td><td rowspan="2"><i>Soluble.</i>
Phosphates.
Add ammonia; white ppt. =phosphate of calcium, or ammonio-magnesium phosphate, or both.</td></tr>
<tr><td><i>Insoluble.</i>
Uric acid.
Apply the murexid test (p. 427.)</td><td><i>Soluble.</i>
Oxalate of calcium.
May be reprecipitated by ammonia.</td></tr>
</table>

Notes.—Urinary deposits are seldom of a complex character: the action of heat and acetic and hydrochloric acids generally at once indicates the character of the deposit, rendering filtration and precipitation unnecessary.

The Urates are often of a pink or red colour, owing to the presence of a pigment termed *purpurin;* hence the common name of *red gravel* for such deposits. *Purpurin* is soluble in alcohol, and may be removed by digesting a red deposit in that solvent. It is seldom necessary to determine whether the urate be that of ammonium, calcium, or sodium (*see* also Uric acid, page 428). The deposited urate is a very acid urate which slowly (more rapidly in urine diluted with water) breaks up into a less acid urate and uric acid (Bence Jones). The occurrence in the urine of the salines of our food, especially of dipotassic phosphate, is apparently (Roberts) what prevents this decomposition before the urine is exposed to the air.

The Phosphate of calcium and the *ammonio-magnesium phosphate* are usually both present in a phosphatic deposit, the magnesium salt forming the larger proportion. They may, if necessary, and if sufficient in quantity, be separated by collecting on a filter, washing, and boiling with solution of carbonate of sodium. The carbonates of calcium and magnesium thus formed are collected on a filter, washed, and dissolved in a drop or two of hydrochloric acid; chloride of ammonium, ammonia, and carbonate of ammonium are added, and the mixture boiled and filtered; any calcium originally present will then remain insoluble, as carbonate of calcium; while any magnesium will be precipitated from the filtrate as ammonio-magnesium phosphate on the addition of phosphate of sodium, the mixture being also well stirred. ——The chief portion of excreted phosphates is carried off by the fæces, that remaining in the urine being kept in solution by the influence of acid phosphate of sodium and, frequently, lactic acid.——Occasionally, an hour or two after a hearty meal, the urine becomes sufficiently alkaline for the phosphates to be deposited, and the urine when passed is turbid from their presence.——The ammoniacal constituent of the magnesium salt does not occur normally, but is produced from urea as soon as urine becomes alkaline.

Oxalate of calcium is seldom met with in excessive amounts, but very often in small quantities mixed with phosphates. In one case of oxaluria the whole urine excreted by a patient in twenty-four hours furnished to the author only two-thirds of a grain of oxalate of calcium.

Free uric acid is in most cases distinctly crystalline, and nearly always of a yellow, red, or brown colour.

Artificial sediments.—For educational practice, these may be obtained as follows:—1. Rub up in a mortar a few grains of serpent's excrement (chiefly urate of ammonium) with an ounce or two of urine; this represents a sediment of urates. 2. Add a few drops of solution of ammonia or solution of carbonate of ammonium to urine; the deposit may be regarded as one of phosphates. 3. To an ounce or two of urine add very small quantitities of chloride of calcium and oxalate of ammonium; the precipitate is oxalate of calcium. 4. To urine acidulated by hydrochloric acid add a little serpent's excrement; the sediment is uric acid.

Other deposits than the foregoing are occasionally observed. Thus *hippuric acid* ($HC_9H_8NO_3$), a normal constituent of human urine, and largely contained in the urine of herbivorous animals, is sometimes found associated with uric acid in urinary sediment, especially in that of patients whose medicine contains benzoic acid (p. 401). Its appearance, as observed by aid of the microscope, is characteristic—namely, slender, four-sided prisms, having pointed ends. *Cystin* ($C_3H_7NSO_2$) (from κύστις, *küstis*, a bladder, in allusion to its origin) rarely occurs as a deposit in urine. It is not soluble in warm urine or dilute acetic acid, and scarcely in diluted hydrochloric acid—hence would be met with in testing for free uric acid. It is very soluble in ammonia, recrystallizing from a drop of the solution placed on a piece of glass in characteristic microscopic six-sided plates. *Leucine* and *tyrosine* (see p. 612) occur in cases of phosphorus poisoning and of acute yellow atrophy of the liver. *Organized sediments* may be due to the corpuscles of pus, mucus, or blood, fat-globules, spermatozoa, cylindrical casts of the tubes of the kidneys, epithelial cells from the walls of the bladder, or foreign matters, such as fibres of wool, or of cotton or wood, small feathers, dust, starch, etc.; these are best recognised by the microscope. (*See* the accompanying Plates, and the following paragraphs on the microscopic appearances of both crystalline and organized urinary sediments.)

Microscopic Examination of Urinary Sediments.

Urine containing insoluble matter is usually more or less opaque. For microscopical examination a few ounces should be set aside in a conical test-glass for an hour or two, the clear supernatant urine poured off from the sediment as far as possible, a small drop of the residue placed on a slip of glass and covered with a piece of thin glass, and examined under the microscope with different magnifying powers.

The respective appearances of the various crystalline and organized matters are given in the annexed Plates (figs. 51 to 62), the figures of which were kindly drawn by the late H. B. Brady, F.R.S., from natural specimens in the collections of St. Bartholomew's Hospital, Dr. Sedgwick, the late Mr. W. W. Stoddart, Mr. Waddington, and the Author.

Uric acid occurs in many forms, most of which are given in the first Plate. Flat, more or less oval crystals, sometimes attached to each other, their outline then resembling an 8, a cross or a star, are common. Single and grouped quadratic prisms, aigrettes, spicula, and crystals recalling dumb-bells are met with. From urine acidulated by hydrochloric acid, square crystals, two opposite sides smooth and two jagged, are generally deposited: acidulated by acetic acid, more typical forms are obtained. A drop of solution of potash or soda placed on the glass slip will dissolve a deposit of uric acid, a drop of any acid reprecipitating it in minute but characteristic crystals.

Cystin is very rarely met with as an urinary deposit; that from which the figure on Plate I. was taken was found in the urine of a patient in St. Bartholomew's Hospital. Lamellæ of cystin always assume the hexagonal character; but the angles are sometimes ill defined and the plates superposed: in the latter case, a drop of solution of ammonia placed on the glass at once dissolves the deposit, well-marked, six-sided crystals appearing as the drop dries up.

Triple phosphate (phosphate of magnesium and ammonium) is deposited as soon as urine becomes alkaline, the ammoniacal constituent being furnished by the decomposition of urea. It occurs in large prismatic crystals, forming a beautiful object when viewed by polarized light,—sometimes also in ragged stellate or arborescent crystals, resembling those of snow. Both forms may be artificially prepared by adding a small lump of carbonate of ammonium to a few ounces of urine and setting aside in a test-glass.

Amorphous deposits are either *earthy phosphates* (a mixture of phosphates of magnesium and calcium) or *urates* of calcium, magnesium, ammonium, potassium, or sodium—chiefly the latter. They may be distinguished by the action of a drop of acetic acid placed near the sediment on the glass slip, the effect being watched under the microscope; phosphates dissolve, while urates gradually assume characteristic forms of uric acid. Urates redissolve when warmed with the supernatant urine.

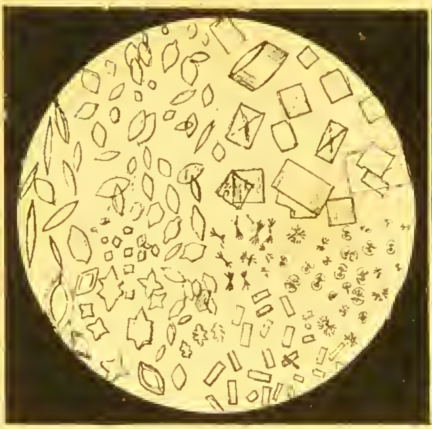
Urates of sodium and magnesium, though generally amorphous, occasionally take a crystalline form—bundles or tufts of small needles—as shown in the Plate. When pink or brick-red, the colour is due to *uroerythrin.*

Oxalate of calcium commonly occurs in octahedra requiring high magnifying-power for their detection. The crystals are easily overlooked if other matters are present, but are more distinctly seen after phosphates have been removed by acetic acid. In certain aspects the smaller crystals look like square plates traversed by a cross. A dumb-bell form of this deposit is also sometimes seen, resembling certain forms of uric acid and the coalescing spherules of a much rarer sediment—carbonate of calcium. Oxalate of calcium is insoluble in acetic but soluble in hydrochloric acid. The octahedra are frequently met with in the urine of persons who have partaken of garden rhubarb and certain other vegetables. The crystals may often be deposited artificially (according to Waddington) by dropping a fragment of oxalic acid into several ounces of urine and setting aside for a few hours.

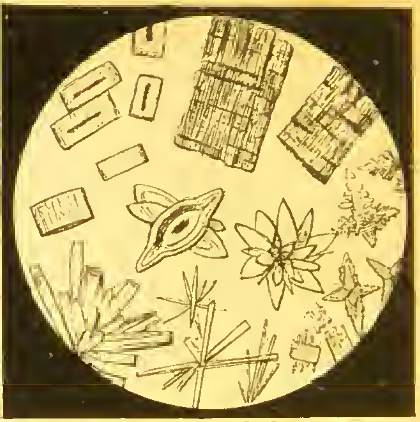
Carbonate of calcium is rarely found in the urine of man, but frequently in that of the horse and other herbivorous animals. Human urine containing carbonate of calcium often reddens litmus-paper; and it is only after the removal, on standing, of the excess of carbonic acid, that the salt is deposited. It consists of minute spherules, varying in size, the smaller ones often in process of coalescence. The dumb-bell form thus produced is easily distinguished from similar groups of uric acid or oxalate of calcium by showing a black cross in each spherule when viewed by polarized light. Acetic acid dissolves carbonate of calcium, liberating carbonic acid gas, with visible effervescence (under the microscope) if the slide has been previously warmed and a group of crystals be attacked.

Hippuric acid.—The pointed rhombic prisms and acicular crystals are characteristic and easily recognised. The broader crystals may possibly be mistaken for triple phosphate, and the narrower for certain forms of uric acid; but insolubility in acetic acid distinguishes them from the former, and solubility in alcohol from the latter. These tests may be applied while the deposit is under microscopic observation. An alcoholic solution of hippuric acid evaporated to dryness, and the residue treated with water, gives a solution from which characteristic crystalline forms of hippuric acid

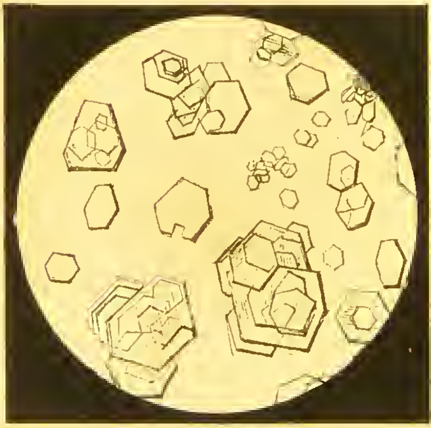
URINARY DEPOSITS. (UNORGANIZED)



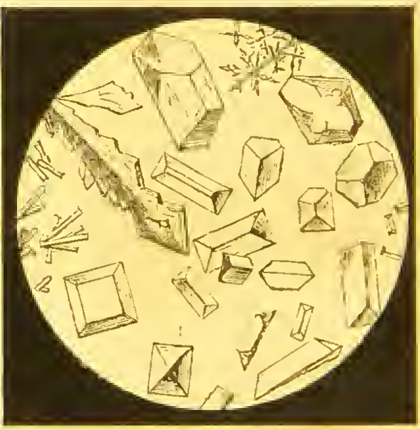
URIC ACID



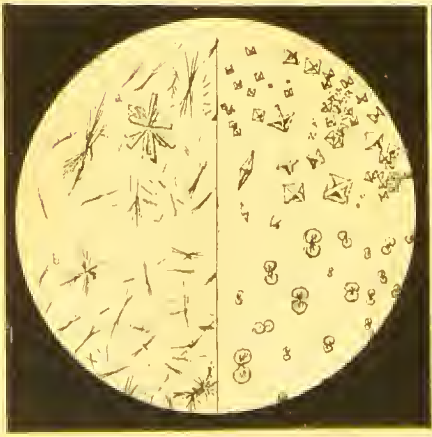
URIC ACID

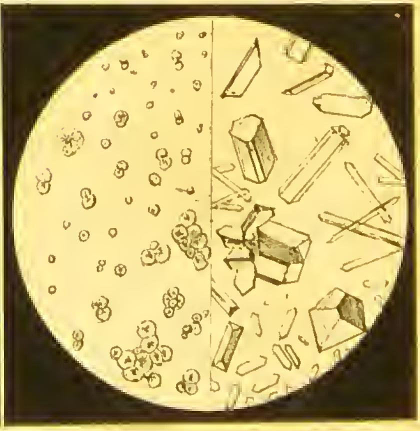


CYSTIN



TRIPLE PHOSPHATE



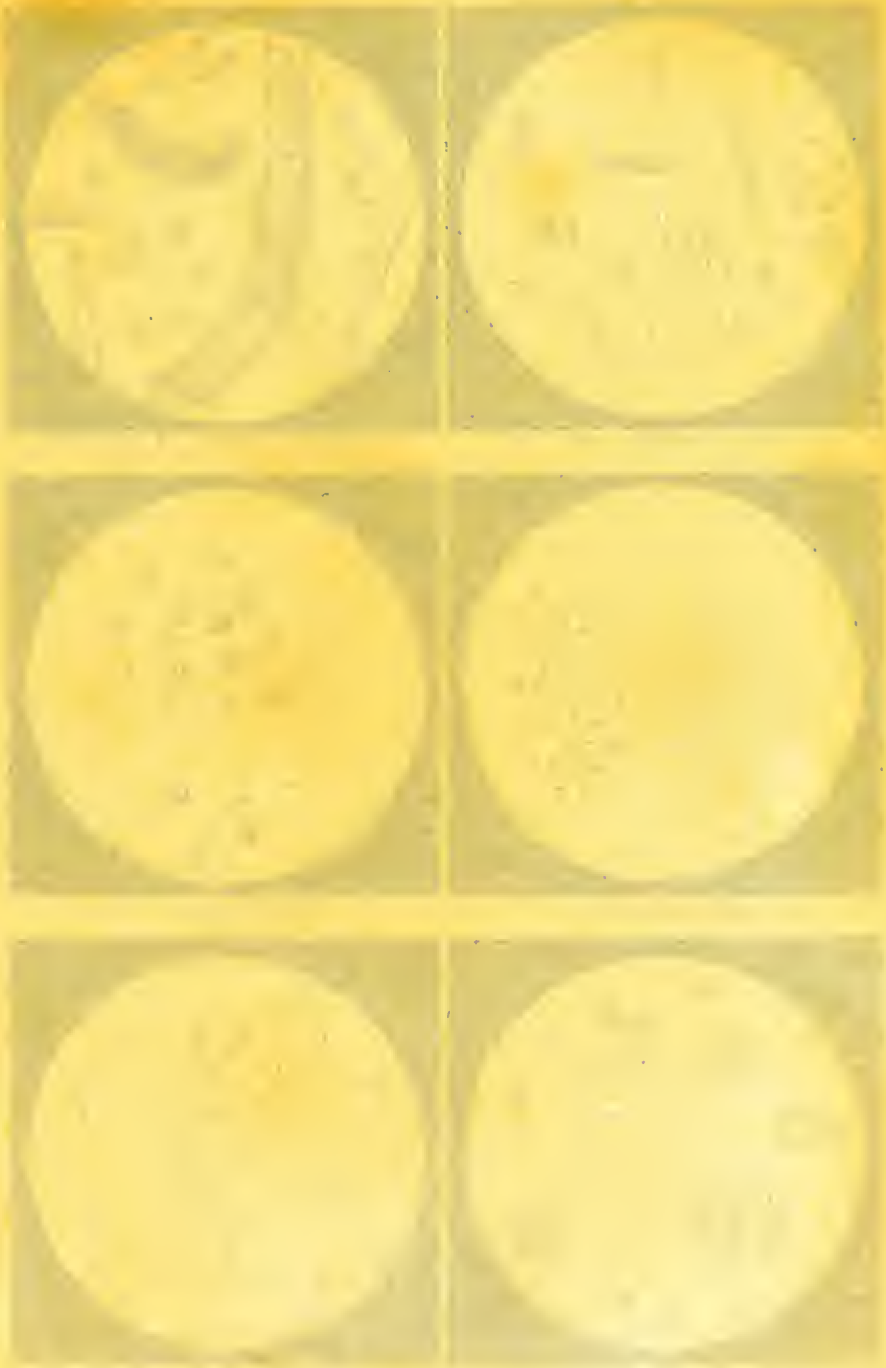


URATES, a of Sodium, b, of Magnesium. OXALATE of CALCIUM. CARB OF CALCIUM HIPPURIC ACID

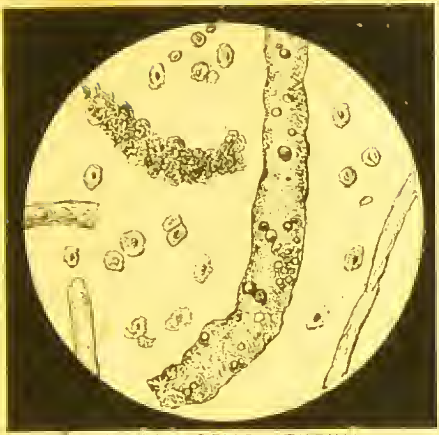
As seen with a ⅔ inch objective & N° 1 eye piece i.e. magnified 60 diam^s

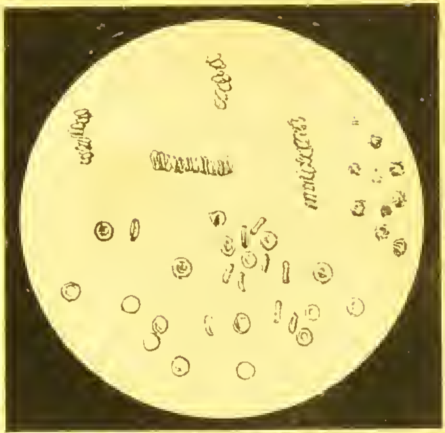
H B Brady del a nat Tuffen West sc

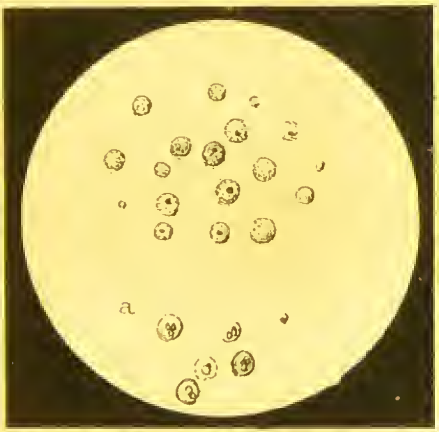
W West imp



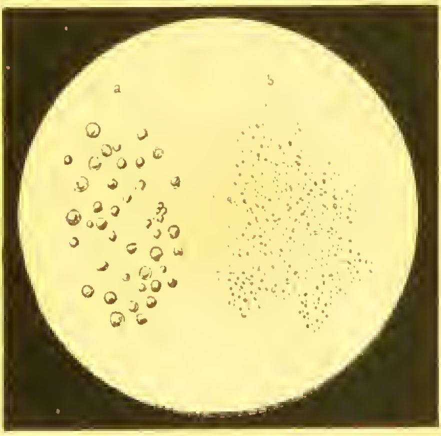
URINARY DEPOSITS (ORGANIZED)


EPITHELIAL CELLS & TUBULI

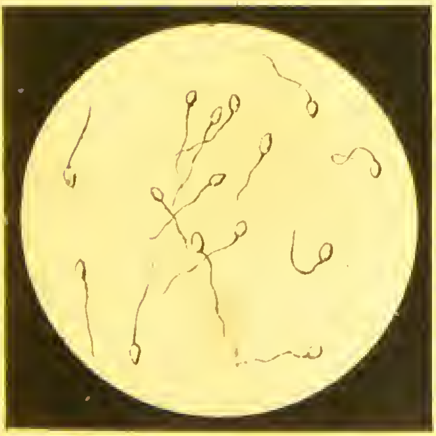

BLOOD CORPUSCLES

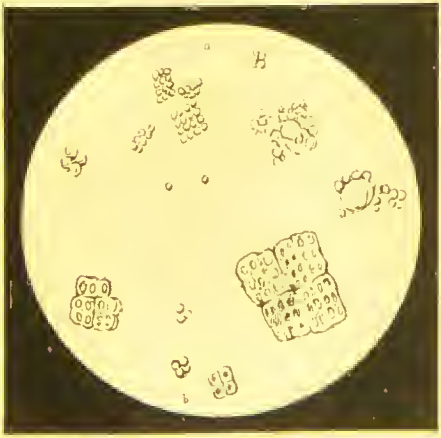


PUS CORPUSCLES



FAT GLOBULES.


SPERMATOZOA



SARCINA VENTRICULI

As seen with a ⅕ inch objective & N°1 eye piece = magnified 230 diam

may be obtained on allowing a drop to dry up on a slip of glass.

Plate II. The organized deposits in urine entail greater care in their determination, and usually require a higher magnifying power for their proper examination than those of crystalline form. The figures on the second of the accompanying Plates are drawn to 230 diameters. The following notes will assist the observer.

Casts of uriniferous tubuli are fibrinous masses of various forms, and often of considerable length—sometimes delicate and transparent, occasionally granular, and often beset with fat-globules. Epithelial *débris* are frequently present in urine in the form of nucleated cells, regular and oval when full, but angular and unsymmetrical when partially emptied of their contents—sometimes perfect, but more frequently a good deal broken up. Casts are very readily discovered by the use of the microscope, if, to a sample of the urine supposed to contain them, best in a conical glass, a few drops of an aniline dye be added. "Carbo-fuchsine" answers well. The casts rapidly stain, and are then quite easily seen in the field.

Blood is easily recognised. Urine containing it is usually high-coloured or "smoky," and the corpuscles appear under the microscope as reddish circular discs, either single or laid together in strings resembling piles of coin. Their colour and somewhat smaller size serve to distinguish them from pus-corpuscles. In doubtful cases a minute drop of blood taken from a finger by help of a needle should be diluted with water and used for comparison. After urine containing blood has stood for some time, the corpuscles lose their regular rounded outline and become crenated. (*See a* in the figure.)

Dr. Day, of Geelong, tests for blood in urine or in stains on clothing by employing a recently prepared alcoholic solution of the inner unoxidized portions of guaiacum resin, and an aqueous or ethereal solution of peroxide of hydrogen, when a dull blue colour results. In the case of urine, add to a drachm or two in a test-tube nearly as much of the ethoreal fluid, and then two or three drops of the guaiacum tincture; on gently agitating the tubo, a bluish-green layer appears at the junction of tho fluids if blood is present. "If tho stain is on a dark-colourod fabric, the parts moistenod by the fluids may be pressed with whito blotting-paper, when bluo impressions will be obtained. Contact with many substances causes the blue reaction or oxidation of guaiacum: the peculiarity of blood is, that it does not produce this effect unless peroxide of hydrogen or a similar 'antozonic' liquid is present. Bodies such as permanganate of potassium, whose oxygen is apparently in the form of ozone, also cause the production of a blue colour with guaiacum; peroxide of hydrogen and other compounds whose oxygen is in the opposite, positive, or, according to Schönbein, antozonic condition, produce no such effect. It would seem as if blood or some constituent of blood has the power of converting positive into negative oxygen, and thus bringing about an effect which negative oxygen alone is able to produce; for of all substances which, like blood, do not alone cause guaiacum to become blue, blood is the only one that affects 'antozonides' (themselves inactive) as to enable them to act as ozonides, that is, to oxidize the guaiacum. Both the venous and arterial fluid from any red-blooded animal will produce this blue reaction. Fruit-stains are darkened by ammonia, which does not alter the colour of blood. Iron-stains or iron-moulds yield no colour to water, whereas the red colouring-matter of blood is soluble in water. The peroxide of hydrogen should be free from more than a trace of acid."

The blood corpuscles of ordinary animals are much smaller than those of man; but a $\frac{1}{16}$ or $\frac{1}{25}$ inch lens is necessary for proper differentiation (J. C. Richardson).

Pus and mucus.—Purulent urine deposits, on standing, a light-coloured layer, easily diffused through the liquid by shaking. Acetic acid does not dissolve the sediment; and solution of potash of official strength converts it into a gelatinous mass. Under the microscope, pus-corpuscles appear rounded and colourless, rather larger than blood-discs, and somewhat granular on the surface. They generally show minute nuclei, which are more distinctly seen after treatment with acetic acid. (*See* the portion of the figure marked *a.*) Mucus possesses no definite microscopic characters, but commonly has imbedded in it pus, epithelium, and air-bubbles. Mucus is coagulated in a characteristic manner by acetic acid; and this reaction, together with the ropy appearance it imparts to urine, prevents it being confounded with pus.

Day's test for pus consists in adding a drop or two of oxidized tincture of guaiacum to the urine or other liquid, when a clear blue colour is produced. It is necessary to moisten dry pus with water before applying the test. The test-liquid is made by exposing a saturated alcoholic solution of guaiacum to the air until it has absorbed a sufficient quantity of oxygen to give it the property of turning green when placed in contact with iodide of potassium. Day's test for mucus consists in the application, first, of oxidized tincture of guaiacum, which by itself undergoes no change in the presence of mucus, and then in the addition of carbolic acid or creasote, which quickly changes the colour of the guaiacum to a bright blue. Neither carbolic acid nor creasote alone will render guaiacum blue. In testing for mucus on cloths, or when it is mixed with blood, it is necessary to use the carbolic acid pure; but when the mucus is in a liquid state, it is better to use carbolic acid diluted with alcohol.

Saliva.—This secretion is an aqueous fluid containing less than 1 per cent. of solid matter, of which one-third is an albumenoid substance termed *ptyalin* (from πτύαλον, *spittle*), a ferment that has the power of converting starch into dextrin and grape-sugar: alkaline salts, including a trace of sulphocyanate of potassium, and calcium compounds, are also present. Day's test for saliva in urine, etc., is similar to that for mucus, with the exception that the blue reaction produced by the oxidized tincture of guaiacum and alcoholic solution of carbolic acid is highly intensified by the addition of a little ethereal or aqueous solution of peroxide of hydrogen.

Fatty matter occurs either as minute globules partially diffused through the urine (as shown at *a*) or in more intimate emulsion (as at *b* in the figure). When present in larger quantity, it collects as a sort of skim on the surface after standing.

Spermatozoa are liable to escape notice, on account of their small size and extreme transparency. Suspected urine should be allowed to settle some hours in a conical test-glass, and the drop at the bottom examined under a high power. The drawing shows their tadpole-like appearance.

Sarcinæ rarely occur in urine, but are not infrequent in vomited matters. The upper figures (*a*) are copied from Dr. Thudichum's drawing (from urine); the larger groupings (*b*) are from vomited matter.

Extraneous bodies, such as starch, hair, wool, fibres of cotton or of deal, or fragments of feathers, are often found in urinary deposits; and ludicrous mistakes have been made by observers not on their guard in respect to such casual admixtures.

EXAMINATION OF URINARY CALCULI.

The term *calculus* is the diminutive of *calx*, a lime- or chalk-stone.

The following calculi have been met with:—(1) Uric acid, (2) Sodium urate, (3) Calcium oxalate (mulberry), (4) Fusible or mixed calcium and triple phosphates, (5) Calcium phosphate, (6) Calcium carbonate, (7) Xanthine, (8) Cystin, (9) Urostealith (fatty matter), (10) Indigo (one case).

Knowledge of the composition of a calculus or urinary deposit affords valuable diagnostic aid to the physician; hence the importance of a trustworthy analysis of these substances.

Nature of calculi.—Urinary calculi have the same composition as unorganized urinary sediments. They consist, in short, of sediments that have been deposited slowly within the bladder, particle on particle, layer on layer, the several substances becoming so compact as to be less easily acted on by reagents than when deposited after the urine has been passed—the urates less readily soluble in warm water, the calcic phosphate insoluble in acetic acid until it has been dissolved in hydrochloric acid and reprecipitated by an alkali.

Preliminary treatment.—If the calculus is whole, saw it in two through the centre, and notice whether it is built up of distinct layers or apparently consists of one substance. If the latter, use about a grain of the sawdust for analysis; if the former, carefully scrape off portions of each layer, and examine them separately. If the calculus is in fragments, select fair specimens of about half a grain or a grain each, and reduce to a fine powder by placing on a hard surface and crushing under the blade of a knife.

Analysis.—Commence the analysis by heating a portion, about the size of a pin's head, on platinum foil, in order to ascertain whether organic matter, inorganic matter, or both are present. If both, the ash is examined for inorganic substances, and a fresh portion of the calculus for uric acid by the murexid test. (In the absence of uric acid any slight charring may be considered to be due to indefinite animal matter.) If composed of organic matter only, the calculus will in nearly all cases be uric acid, the indication being confirmed by applying the murexid test in a watch-glass to another fragment, half the size of a small pin's head. If inorganic only, the ash on the platinum foil may be examined for phosphates, and a separate portion of the calculus for oxalates. Even a single drop of liquid obtained in any of these experiments may be filtered by placing it on a filter not larger than a sixpence and previously moistened with water, and adding three or four drops of water, one after the other as each passes through the paper; or a drop of mixture may be placed on a fragment of damped filter-paper on a glass slide, the latter then tilted, and a clear drop be drained off from the paper on to the slide ready for the addition of a reagent. If the calculus is suspected to contain more than one substance, boil about half a grain of the powder in half a test-tubeful of distilled water for a few minutes and pour it on a small filter; then proceed according to the following Table:—

<table>
<tr><td colspan="3">*Insoluble.*
Phosphates, oxalate of calcium, and free uric acid.
Boil with two or three drops of hydrochloric acid, and filter.</td><td rowspan="3">*Soluble.*
Urates.
These will probably be redeposited as the solution cools. Small quantities may be detected by evaporating the solution to dryness. They are tested for ammonium, sodium, calcium, and the uric radical by the appropriate reagents.</td></tr>
<tr><td rowspan="2">*Insoluble.*
Uric acid. Apply the murexid test (p. 427).</td><td colspan="2">*Soluble.*
Phosphates and oxalate of calcium.
Add excess of ammonia, and then excess of acetic acid; filter.</td></tr>
<tr><td>*Insoluble.*
Oxalate of calcium.</td><td>*Soluble.*
Phosphates.
They may be re-pptd. by ammonia.</td></tr>
</table>

Varieties of calculi.—Calculi composed entirely of *uric acid* are common; a minute portion heated on platinum foil chars, burns, and leaves scarcely a trace of ash. The phosphates frequently occur together, forming what is known as the *fusible calculus*, from the readiness with which a fragment aggregates, and even fuses to a bead, when heated on a loop of platinum wire in the blowpipe-flame. The phosphates may, if necessary, be further examined by the method described in connection with urinary deposits. Oxalate of calcium often occurs alone, forming a dark-coloured calculus having a very rough surface, hence termed the *mulberry calculus*. Smaller calculi of the same substance are called, from their appearance, *hempseed calculi*. Calculi of *cystin* are rarely met with. *Xanthine* (from ξανθὸς, *xanthos*, yellow, in allusion to the colour it yields with nitric acid) still less often occurs as a calculus. The earthy concretions, or "*chalk-stones*," which frequently form in the joints of gouty persons are composed chiefly of urates, the sodium salt being that most commonly met with. *Gall-stones*, or *biliary calculi*, occasionally form in the gall-bladder; they contain *cholesterin* (from χολὴ, *cholē*, bile, and στερεὸς, *stereos*, solid), a fatty substance of alcoholoid constitution, soluble in rectified spirit or ether, and crystallizing from such solutions in well-defined, square, scaly crystals. Phosphatic and other calculi of many pounds weight are occasionally found in the stomach and larger intestines of animals.

QUESTIONS AND EXERCISES.

In breathing, how much carbon (in the form of carbonic acid gas) is exhaled from the lungs every 24 hours?—How may the presence of carbonic acid gas in expired air be demonstrated?—Mention an experiment showing the escape of moisture from the lungs during breathing.—State the method of testing for albumen in urine.—Give the tests for sugar in urine.—What is the average composition of healthy urine?—Give the tests for urea.—Write the rational formulæ of some compound ureas in which methyl or ethyl displaces hydrogen.—Describe an artificial process for the production of urea, giving equations.—Sketch out a plan for the chemical examination of urinary sediments.—A deposit is insoluble in the supernatant urine or in acetic acid; of what substances may it consist?—Which compounds are indicated when a deposit redissolves on warming it with the supernatant urine?—Name the salts insoluble in warmed urine, but dissolved on the addition of acetic acid.—Mention the chemical characters of cystin. At what stage of analysis would it be recognised?—Describe the microscopical appearances of the following urinary deposits:—uric acid, cystin, triple phosphate, earthy phosphates, urates, oxalate of calcium, carbonate of calcium, hippuric acid, tube-casts, epithelial *débris*, blood, pus, mucus, fat, spermatozoa, sarcinæ, extraneous bodies.—How are Day's tests for blood, pus, and saliva applied?—State the physical and chemical characters of urinary calculi.—How are urinary calculi prepared for chemical examination?—Draw out a chart for the chemical examination of urinary calculi.—Why is the "fusible calculus" so called? and what is its composition?—State the characters of "mulberry" and "hempseed" calculi.—What are "chalk-stones" of gout, and "gall-stones" or "biliary calculi"?

THE GALENICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA.

The preparation of Cerates, Confections, Decoctions, Enemas, Extracts, Glycerines, Infusions, Inhalations, Juices, Liniments, Lozenges, Mixtures, Ointments, Pills, Plasters, Poultices, Powders, Spirits, Suppositories, Syrups, Tinctures, and Wines, includes a number of mechanical rather than chemical operations, and belongs to the domain of pure Pharmacy. The medical or pharmaceutical pupil will probably have had some opportunity of practically studying these compounds before working at experimental chemistry, and may have prepared many of them according to the directions of the Pharmacopœia; if not, he is referred to the pages of the last edition of that work for details.

Among the extracts, however, there are five (namely, those of Aconite, Belladonna, Hemlock, Henbane, and Lettuce) which are not simply evaporated infusions, decoctions, or tinctures, like most others, but are evaporated juices from which vegetable albumen, the supposed source of fermentation and decay has been removed, and chlorophyll (the green colouring-matter of plant-juice) retained practically unimpaired in tint. For educational practice either of the above-named five raw materials may be employed; but in order that attention may be concentrated on the process by which the extracts are prepared, rather than on any one of the extracts themselves, it suffices to make an extract of some ordinary green vegetable, such as cabbage or turnip-tops. Bruise the green leaves of a good-sized cabbage in a mortar, and press out the juice; heat it gradually to 130° F., and remove the green flocks of chlorophyll which separato, by filtration through calico. When the liquor has all passed through the filter, set the chlorophyll aside for a time, heat the strained liquor to 200° F. to coagulate albumen; remove the latter by filtration and throw it away; evaporate the filtrate on a water-bath to the consistence of thin syrup; then add to it the chlorophyll, first passing the latter through a hair sieve, to break up clots, and, stirring the whole together assiduously, continue the evaporation at a temperature not exceeding 140° F., until the extract is of a suitable consistence for forming pills. A higher temperature than that indicated would cause the alteration of the chlorophyll to a dark-brown substance, any such extract used in pharmacy no longer having the green tint which custom and the British Pharmacopœia demand.

QUESTIONS AND EXERCISES.

Enumerate the different classes into which official galenical preparations may be divided.—Describe the general process for the preparation of green extracts:—aconite, belladonna, hemlock, henbane, lettuce.—Why is vegetable albumen excluded in the preparation of green extracts?—How may chlorophyll be removed from vegetable juices, and again be introduced into their evaporated residues, without destroying its colour?—For what reason is exposure of chlorophyll to a boiling temperature avoided in the manufacture of green extracts?

THE CHEMICAL PREPARATIONS OF THE BRITISH PHARMACOPŒIA.

The process by which every official chemical substance is prepared has already been described, and the strictly chemical character of the processes illustrated by experiments and explained by aid of equations. Should the reader, in addition, desire an intimate acquaintance with those details of manipulation on which the successful and economic manufacture of chemical substances depends, he is advised to prepare, if he has not done so already, a few ounces of each of the salts mentioned in the British Pharmacopœia or commonly used in Pharmacy. An additional guide in these operations will be the Pharmacopœia itself.

The production of many chemical and galenical substances on a commercial scale can only be successfully carried on in manufacturing laboratories, and with some knowledge of the circumstances of supply and demand, value of raw material, and by-products, etc.; for the technical preparation of such substances requires much knowledge beyond even a thorough acquaintance with chemistry. Still, in the present day, commercial Chemistry and Pharmacy can best hope for success when founded on the working out of abstract scientific principles. The problem of manufacturing success is now only solved with certainty by sound and wisely-applied science.

Memorandum.—The next subjects of experimental study will be determined by the nature of the student's future pursuits. In most cases the operations of quantitative analysis will engage attention. These should be of a volumetric and gravimetric character; for details concerning them, see the following pages.

QUANTITATIVE ANALYSIS.

INTRODUCTORY REMARKS.

General Principles.—The proportions in which chemical substances unite with each other in forming compounds are definite and invariable (p. 45). Quantitative analysis is based on this law. When, for example, aqueous solutions of a salt of silver and a chloride are mixed, a white curdy precipitate is produced containing chlorine and silver in atomic proportions—that is, 35·5 parts of chlorine to 108 of silver. No matter what the chloride or what the salt of silver, the resulting chloride of silver is invariable in composition. The formula AgCl is a convenient picture of this compound in these proportions. The weight of a definite compound being given, therefore, the proportional amounts of its constituents can be ascertained by simple calculation. Suppose, for instance, 8·53 parts of chloride of silver have been obtained in some analytical operation: this amount will contain 2·11 parts of chlorine and 6·42 of silver. For if 143·5 (the molecular weight) of chloride of silver contain 35·5 (the atomic weight) of chlorine, 8·53 of chloride of silver will be found to contain 2·11 of chlorine:—

143·5 : 35·5 :: 8·53 : x
8·53
———
1·065
17·75
284·0
———
143·5)302·815(2·11
287·0
———
15·81
14·35
———
1·465
1·435 $x = 2·11$

And if 143·5 of chloride of silver contain 108 of silver, 8·53 of chloride of silver will contain 6·42 of silver. To ascertain, for example, the amount of silver in a substance containing, say, nitrate of silver, all that is necessary is to take a weighed quantity of the substance, dissolve it, precipitate the whole of the silver by adding hydrochloric acid or other chloride till no more chloride of silver falls, collect the precipitate on a filter, wash, dry, and weigh. The amount of silver in the dried chloride, ascertained by calculation, is the amount of silver in the quantity of substance on which the operation was conducted; a rule-of-three sum gives the quantity per cent.—the form in which the results of quantitative analyses are usually stated. Occasionally a constituent of a substance admits of being isolated and weighed in the uncombined state. Thus the amount of mercury in a substance may be determined by separating and weighing the mercury in the metallic condition; if occurring as calomel ($HgCl$) or corrosive sublimate ($HgCl_2$), the proportion of chlorine may then be ascertained by calculation ($Hg = 200$; $Cl = 35{\cdot}5$).

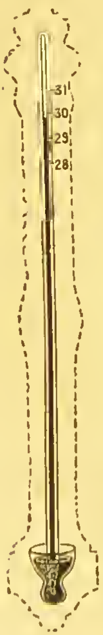
Nature of Gravimetric Quantitative Analysis.—As above stated, a body may be isolated and *weighed* and its quantity thus ascertained; or it may be separated and weighed in combination with another body whose combining proportion is well known; this is quantitative analysis by the *gravimetric* method.

Nature of Volumetric Quantitative Analysis.—Volumetric operations depend for success on some accurate initial gravimetric operation. A *weighed* amount of a pure salt is dissolved in a given *volume* of water or other fluid, and thus forms *a standard solution.* Accurately *measured* quantities of such a solution will obviously contain just as definite amounts of the dissolved salt as if those amounts were actually *weighed* in a balance; and as measuring occupies less time than weighing, the volumetric operations can be conducted with great economy of time as compared with the corresponding gravimetric operations. Quantitative analysis by the *volumetric* method consists in noting the volume of the standard liquid required to be added to the substance under examination before a given effect is produced. Thus, for instance, a solution of nitrate of silver of known strength may be used in experimentally ascertaining an unknown amount of a chloride in any substance. The silver solution is added to a solution of a definite quantity of the substance until flocks of chloride of silver cease to be precipitated: every 108 parts of silver added (or 170 of nitrate of silver: $Ag = 108$, $N = 14$, $O_3 = 48$; total 170) indicate the presence of 35·5 of chlorine, or an equivalent quantity of any chloride. The preparation of a standard solution, such as that of the nitrate of silver to which allusion is here made, requires much care; but once it is prepared, certain analyses can, as already indicated, be executed with far more rapidity and ease than by gravimetric processes.

Quantitative Determination of (a) Atmospheric Pressure, (b) Temperature, and (c) Weight.—The analysis of solids and liquids often involves quantitative determinations not only of weight, as just indicated, but of temperature and atmospheric pressure. The two latter processes will now be explained, after which an outline of volumetric and gravimetric quantitative analysis will be given. The scope of this work precludes any attempt to describe all the little mechanical details observed by quantitative analysts; essential operations, however, are so fully treated that expert manipulators will meet with little difficulty.

QUANTITATIVE DETERMINATION OF ATMOSPHERIC PRESSURE.

Fig. 63.

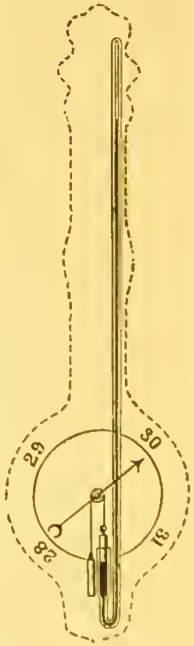


BAROMETER.

The Barometer.—The analysis of gases and vapours involves determinations of the varying pressure of the atmosphere as indicated by the *barometer* (from βάρος, *baros*, weight, and μέτρον, *metron*, measure).

The ordinary mercurial barometer is a glass tube 33 or 34 inches long, closed at one end, filled with mercury, and inverted in a small cistern or cup of mercury (fig. 63). The mercury remains in the tube, owing to the weight or pressure of the atmosphere on the exposed surface of the liquid, the average height of the column being nearly 30 inches. In the popular form of the instrument, the wheel barometer, the cistern is formed by a recurvature of the tube (fig. 64); on the exposed surface of the mer-

Fig. 64.



BAROMETER.

cury a float is placed, from which a thread passes over a pulley and moves an index whenever the column of mercury rises or falls. As supplied to the public, these barometers are usually enclosed in ornamental frames with thermometers attached. In the wheel barometer the glass tube and contained column of mercury are altogether enclosed, the index alone being visible. In the other variety the upper end of the glass tube and mercurial column are exposed, and the height of the mercury is ascertained by direct observation.

The aneroid barometer (from ἀ, *a*, without, and νηρὸς, *nēros*, fluid) consists of a small shallow vacuous metal drum, the sides of which approach each other when an increase of atmospheric pressure occurs, their elasticity enabling them to recede towards their former position on a decrease of pressure. This motion is so multiplied and altered in direction by levers, etc., as to act on a hand traversing a plate on which are marked numbers corresponding with those showing the height of the mercurial column of the ordinary barometer by which the aneroid was adjusted. *The Bourdon barometer* (from the name of the inventor) is a modified aneroid, containing in the place of the round metal box a flattened vacuous tube of metal bent nearly to a circle. These barometers are also useful for measuring the pressure in steam-boilers, etc. Under the name of *pressure-gauges* they are sold to indicate pressure of 500 pounds per square inch and upwards. From their portability (they can be made of 1 to 2 inches in diameter and less than an inch thick) they are handy companions for travellers wishing to know the heights of hills, mountains, and other elevations.

For further information concerning the influence of pressure on the volume of a gas or vapour, *see* p. 731; and for descriptions of the methods of analysing gases, refer to Ganot's "Physics" (translated by Atkinson), Miller's "Chemical Physics," and "Analysis of Gases" in Watts's "Dictionary of Chemistry."

QUANTITATIVE DETERMINATION OF TEMPERATURE.

General Principles.—As a rule, all bodies expand on the addition, and contract on the abstraction, of heat, the alteration in volume being constant and regular for equal increments or decrements of temperature. The extent of this alteration in a given substance, expressed in parts or degrees, constitutes the usual method of intelligibly stating with accuracy, precision, and minuteness a particular condition of warmth or temperature—that is, of sensible heat. The substance commonly employed for this purpose is mercury, the chief advantages of which are, that it will bear a high temperature without boiling, a low temperature without freezing, does not adhere to glass to a sufficient extent to "wet" the sides of any tube in which it may be enclosed, and, from its good conducting-power for heat, responds rapidly to changes of temperature. Platinum, earthenware, alcohol, and air are also occasionally used for thermometric purposes.

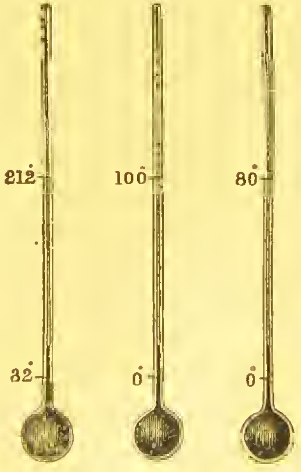
The Thermometer.—The construction of an accurate thermometer is a matter of great difficulty; but the following are the leading steps in the operation. Select a piece of glass tubing having a fine capillary (*capillus*, a hair) bore, and about a foot long; heat one extremity in the blowpipe-flame until the orifice closes, and the glass is sufficiently soft to admit of a bulb being blown; heat the bulb to expel air, immediately plunging the open extremity of the tube into mercury; the bulb having cooled, and some mercury having entered and taken the place of expelled air, again heat the bulb and tube until the mercury boils and its vapour escapes through the bore of the tube; again plunge the extremity under mercury, which will probably now completely fill the bulb and tube. When cold, the bulb is placed in melting ice. The top of the column of mercury in the capillary tube should then be within an inch or two of the bulb; if higher, some of the mercury must be expelled by heat; if lower, more metal must be introduced as before. The tube is now heated near the open end and a portion drawn out, until the diameter is reduced to about one-tenth. The bulb is next warmed until the mercurial column rises above the constricted part of the tube, which is then rapidly fused in the blowpipe-flame, and the extremity of the tube removed.

The instrument is now ready for *graduation*. The bulb is placed in the steam just above some rapidly boiling water (a medium having, *cæteris paribus*, an invariable temperature), and when the position of the top of the mercurial column is constant (the flask containing the water and steam being jacketed to prevent loss of heat by radiation), a mark is made on the stem by a scratching diamond or a file. This operation is repeated with melting ice (also a medium having an invariable temperature). The space between these two marks is divided into a certain number of intervals termed *degrees.* Unfortunately, this number is not uniform in all countries: in England it is 180, as proposed by Fahrenheit; in France 100, as proposed by Celsius (the Centigrade scale) a number generally adopted by scientific men: in some parts of the Continent the divisions are 80 for the same interval, as suggested by Réaumur. Whichever be the number selected, similar markings should be continued beyond the boiling and freezing points as far as the length of the stem admits. They may be made on the stem itself, or on any wood, metal, or earthenware frame on which the stem is mounted.

Thermometric Scales (Fig. 65).—On the Centigrade (C.) and Réaumur (R.) scales the freezing-point of water is made zero, and the boiling-point 100 and 80 respectively; on the Fahrenheit (F.) scale the zero is placed 32 degrees below the congealing-point of water, the boiling-point of which becomes, consequently, 212. Even on the Fahrenheit system temperatures below the freezing-point of water are often spoken of as "degrees of frost"; thus 19° as marked on the thermometer would be regarded as "13 degrees of frost." It is to be regretted that the freezing-point of water is not universally regarded as the zero-point, and that the number of intervals between that and the boiling-point is not everywhere the same.

Fig. 65.

THERMOMETRIC SCALES.



Fahrenheit. Centigrade. Réaumur.

The degrees of one scale are easily converted into those of *another* if their relations be remembered, namely: 180 (F.), 100 (C.), 80 (R.); or 18, 10, and 8; or best, 9, 5, and 4.

Formulæ for the Conversion of Degrees of one Thermometric Scale into those of Another.

F. = Fahrenheit.
C. = Centigrade.
R. = Réaumur.
D. = The observed degree.

If above the freezing-point of water (32° F.; 0° C.; 0° R.):—

F. into C.	$(D-32)\div 9\times 5$.
F. ,, R.	$(D-32)\div 9\times 4$.
C. ,, F.	$D\div 5\times 9+32$.
R. ,, F.	$D\div 4\times 9+32$.

If below freezing, but above 0° F. (−17·77° C.; −14·22° R.):—

F. into C.	$-(32-D)\div 9\times 5$.
F. ,, R.	$-(32-D)\div 9\times 4$.
C. ,, F.	$32-(D\div 5\times 9)$.
R. ,, F.	$32-(D\div 4\times 9)$.

If below 0° F. (−17·77° C.; −14·22° R.):—

F. into C.	$-(D+32)\div 9\times 5$.
F. ,, R.	$-(D+32)\div 9\times 4$.
C. ,, F.	$-(D\div 5\times 9)-32$.
R. ,, F.	$-(D\div 4\times 9)-32$.

For all degrees:—

C. into R.	$D\div 5\times 4$.
R. ,, C.	$D\div 4\times 5$.

In ascertaining the temperature of a liquid, the bulb of a thermometer is simply inserted and the degree noted. In determining the boiling-point, also, the bulb is inserted in the liquid, if a pure substance. In taking the boiling-point of a substance which is being distilled from a mixture, the bulb of the thermometer should be in the vapour but not beneath nor very near to the surface of the boiling liquid.

The "boiling-point" of a liquid is the temperature at which the elasticity of the vapour of the substance overcomes the atmospheric or other pressure to which the liquid is exposed. If the pressure is equal to 760 mm. (29·92 inches) of mercury, water will boil at 100° C. (212 F.). The boiling-point of a drop of a fluid is taken by introducing it into the closed extremity of a small U tube, the remaining portion of the closed limb being filled with mercury. The tube is lowered into a bath, the open limb being above the surface of the fluid of the bath. The bath is slowly and equally heated, and the boiling-point of the liquid, indicated by the mercury falling until it is level in the two limbs, taken by a thermometer whose bulb is close to the U tube.

The following are the boiling-points of a few substances met with in pharmacy:—

	Centigrade.	Fahrenheit.
Alcohol, absolute	78·3	173
,, 84 per cent.	79·5	175
,, 49 per cent. (proof spirit)	81·4	178·5
,, amylic	132·2	270
Benzol	80·6	177
Bromine (below)	63	145·4
Benzoic acid	239·0	462
Carbolic acid	187·8	370
Chloroform	61	142
Ether (B.P.) (below)	40·5	105
,, pure	35	95
Mercury *in vacuo* (as in a thermometer)	304	580
" in air (barom. at 30 inches)	350	662
Water (barom. at 29·92 inches)	100	212
,, (,, 29·33 ,,)	99·5	211
,, (,, 28·74 ,,)	99	210
Saturated solutions of:—		
Cream of tartar	101	214
Common salt	106·6	224
Sal-ammoniac	113·3	236
Nitrate of sodium	119	246
Acetate of sodium	124·4	256
Chloride of calcium	179·4	355

To determine Melting-Points of Fats.—To melt at a given temperature is a *constant* property of a substance; therefore a melting-point, once it is accurately determined, becomes a valuable indicator of purity in a substance. Heat a fragment of the substance (spermaceti or wax, for example) till it liquefies, and then draw up a small portion into a thin glass tube, about the size of a knitting-needle. Immerse the tube in cold water contained in a beaker, and slowly heat the vessel till the thin opaque cylinder of solid fat melts and becomes transparent; a delicate thermometer placed in the water indicates the point of change to the fifth of a degree. Remove the source of heat, and note the congealing point of the substance; it will, in nearly all cases, be identical with or close to the melting-point.

The following are melting-points of substances official in the British Pharmacopœia :—

	In degrees Centigrade.	In degrees Fahrenheit.
Acetic acid, glacial	8·9	48
,, ,, congeals at	1·1	34
Benzoic acid	120	248
Carbolic acid	35	95
Oil of theobroma (about)	32	90
Phosphorus	43·3	110
Prepared lard (about)	38	100
,, suet	39·5	103
Spermaceti	44 to 50	111 to 122
White wax	63·3	146
Yellow wax	63·3	146

Pyrometers.—Temperatures above the boiling point of mercury are determined by ascertaining to what extent a bar of platinum or porcelain has elongated. The bar is enclosed in a cavity of a suitable case, a plug of platinum or porcelain placed at one end of the bar, and the whole exposed in the region the temperature of which is to be found. After cooling, the distance to which the bar has forced the plug along the cavity is accurately measured and the corresponding degree of temperature noted. The value of the distance is fixed for low temperatures by comparison with a mercurial thermometer, and the scale carried upwards through intervals of equivalent length. Such thermometers are conventionally distinguished from ordinary instruments by the name *pyrometer* (from πῦρ, *pur*, fire, and μέτρον, *metron*, measure).

The order of fusibility of a few of the metals is as follows :—

	In degrees Centigrade.	In degrees Fahrenheit.
Mercury	− 39·4	− 39
Potassium	+ 62·5	+ 144·5
Sodium	97·6	207·7
Tin	227·8	442
Bismuth	264	507
Lead	325	617
Zinc	411·6	773
Antimony	621	1150
Silver	1023	1873
Copper	1091	1996
Gold	1102	2016
Cast iron	1530	2786

QUESTIONS AND EXERCISES.

On what fundamental laws are the operations of quantitative analysis based?—What is the general nature of *gravimetric* quantitative analysis?—Describe the general principle of *volumetric* quantitative analysis.—How are variations in atmospheric pressure determined?—Explain the construction and mode of action of barometers.—In what respect does a wheel-barometer differ from an instrument in which the readings are taken from the top of the column of mercury?—Describe the principles of action of an aneroid barometer.—On what general principles are thermometers constructed?—What material is employed in making thermometers?—Why is mercury selected as a thermometric indicator?—Describe the manufacture of a mercurial thermometer.—How are thermometers graduated?—Give formulæ for the conversion of the degrees of one thermometric scale into those of another, (*a*) when the temperature is above the freezing-point of water, (*b*) below 32° F. but above 0° F., and (*c*) below 0° F.—Name the degree C. equivalent to 60° F.—What degree C. is represented by - 4° F.?—Mention the degree F. indicated by 20° C.—Convert 100° R. into degrees C. and F.—State the boiling-points of alcohol, chloroform, ether, mercury, and water on either thermometric scale.—Describe the details of manipulation in estimating the melting-points of fats.—In what respect do pyrometers differ from thermometers?—Mention the melting-points of glacial acetic acid, oil of theobroma, lard, suet, and wax.—Give the fusing-points of tin, lead, zinc, copper, and cast iron.

QUANTITATIVE DETERMINATION OF WEIGHT.

All bodies, celestial and terrestrial, attract each other, the amount of attraction being in direct proportion to the quantity of matter of which they consist, and in inverse proportion to the squares of their distances. This is *gravitation*. When gravitation in certain directions is exactly counterbalanced by gravitation in opposite directions, a body (*e.g.* the earth) remains suspended in space. Such a body, in relation to other bodies, has gravity but not weight. *Weight* is the effect of gravity, being the excess of gravitation in one direction over and above that exerted in the opposite direction. Weight, truly, in any terrestrial substance, is the excess of attraction which it and the earth have for each other over and above the attraction of each in opposite directions by the various heavenly bodies. But, practically, the weight of any terrestrial substance is the effect of the attraction of the earth only. *Specific weight* is the definite or precise weight of a body in relation to its bulk; it is more usually but not quite correctly termed *specific gravity*—gravity belonging to the earth, and not, in any sensible degree, to the substance.*

QUESTIONS AND EXERCISES.

What is understood by gravitation?—State the difference between weight and gravity.—Mention a case in which a body has gravity but no apparent weight.—Practically, what causes the weight of terrestrial substances?

Weights and Measures.

The Balance.—The balance used in the quantitative operations of analytical chemistry must be accurate and sensitive. The points of suspension of the beam and pan should be polished steel or agate knife-edges, working on agate planes. It should turn easily and quickly, without too much oscillation, to $\frac{1}{500}$ or $\frac{1}{600}$ of a grain, or $\frac{1}{10}$ of a milligramme, when 1,000 grains, or 50 or 60 grammes, are placed in each pan. (Grammes are weights of the metric system, a description of which is given on the next two or three pages.) The beam should be light but strong, capable of supporting a load of 1,500 grains or 100 grammes: its oscillations are observed by help of a long index attached to its centre, and continued downwards for some distance in front of the supporting pillar of the balance. The instrument should be provided with screws for purposes of adjustment, a mechanical contrivance for supporting the beam above its bearings when not in use or during the removal or addition of weights, spiritlevels to enable the operator to give it a horizontal position, and be enclosed in a glass case to protect it from dust. It should be placed in a room the atmosphere of which is not liable to be contaminated by acid fumes, in a situation as free as possible from vibration; and a vessel containing lumps of quicklime should be placed in the case to keep the enclosed air dry and prevent the formation of rust on any steel knife-edges or other parts. During weighing, the doors of the balance should be shut, in order that currents of air may not unequally influence the pans.

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* It must be remembered, also, that centrifugal influence and gravitation are antagonistic.

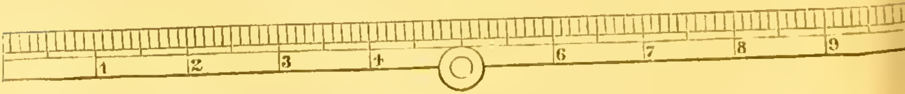
The Weights.—These should be preserved in a box having a separate compartment for each. They must not be lifted directly with the fingers, but by a small pair of forceps. If grain-weights, they should range from 1,000 gr. to $\frac{1}{10}$ gr., a $\frac{1}{10}$ weight being fashioned of gold wire to act as a "rider" on the divided beam, and thus indicate by its position 100ths and 1000ths of a grain. From $\frac{1}{10}$ to 10 grs. the weights may be of platinum or aluminium; thence upwards to 1,000 grains of brass. The relation of the weights to each other should be decimal. Metric decimal weights may range from 100 grammes to 1 gramme, of brass, and thence downwards to 1 centigramme, of platinum or aluminium, a gold centigramme rider being employed to indicate milligrammes and tenths of a milligramme.

The Metric System of weights (the word *metric* is from the Greek *μέτρον*, *metron*, measure) is greatly to be preferred to the British, the relation of the metric weights of all denominations to measures of length, capacity, and surface being so simple as to be within the perfect comprehension of a child; while under the British plan the weights have no such relation, either with each other or with the various measures. Moreover, the metric system is in perfect harmony with the universal method of counting; it is a decimal system.

[It is perhaps impossible to realize, much more express, the advantages we enjoy from the fact that in every country of the world the system of numeration is identical. That system is the decimal. Whatever language a man speaks, his method of numbering is decimal; his talk concerning numbers is decimal; his written or printed signs signifying number are decimal. With the figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 0, he represents all possible variations in number, the position of a figure in reference to its companions alone determining its value, a figure on the left hand of any other figure in an allocation of numeral symbols (for example, 1893) having ten times the value of that figure, while the figure on the right hand of any other has a tenth of the value of that other. When the youngest pupil is asked how many units there are in 1893, he smiles at the simplicity of the question, and says, 1893. How many tens? 189 and 3 over. How many hundreds? 18 and 93 over. How many thousands? 1 and 893 over. But if he is asked how many scruples there are in 1893 grains, how many drachms, how many ounces—he brings out his slate and pencil. And so with the pints or gallons in 1893 fluid ounces, or the feet and yards in 1893 inches, or the pence, shillings, and pounds in 1893 farthings; to say nothing of cross-questions, such as the value of 1893 articles at 9*s.* 6*d.* per dozen, or of the perplexity caused by the varying values of several individual weights or of measures of length, capacity, and surface in different parts of the country. What is desired is, that there should be an equally simple decimal relation among weights and measures and coins as already universally exists among numbers. This condition of things having already been introduced into most other countries, there is no good reason why it should not, in due time, be accomplished in our own. The difficulty in the way consists in requiring, more or less suddonly, every one of the many millions of persons in the country to relinquish the lifelong use of words expressive of the hourly wants of life, such words as pounds, pints, pence, etc., for words such as kilos, litres, cents, etc., which will not express those wants until after weeks or months or perhaps years. The difficulty is one that explanation cannot meet, for it is one of *association* which time alone can resolve, at all events for the great mass of people. Still, "what man has done man can do."]

The system of weights and measures legalized by "the Metric Weights and Measures Act, 1864" is founded on the mètre. Fig. 66 represents a pocket folding measure the tenth part of a mètre in length, divided into 10 centimètres, and each contimètre into 10 millimètres.

Fig. 66.



THE DÉCIMÈTRE.

The units of the system, with their multiples and submultiples, are as follows:—

Length.—The *Unit of Length* is the Mètre, derived from the measurement of the Quadrant of a Meridian of the Earth. (Practically, it is the length of certain carefully preserved bars of metal, from which copies have been taken.)

Surface.—The *Unit of Surface* is the Are, which is the square of Ten Mètres.

Capacity.—The *Unit of Capacity* is the Litre, which is the Cube of a Tenth part of a Mètre.

Weight.—The *Unit of Weight* is the Gramme, which is the Weight of that quantity of Distilled Water, at its maximum density, which fills a Cube of the One-hundredth part of the Mètre.

Table.

Note.—Multiples are denoted by the Greek words "Deka," Ten, "Hecto," Hundred, "Kilo," Thousand.
Subdivisions by the Latin words, "Deci," One-Tenth, "Centi," One-hundredth, "Milli," One-thousandth.

Quantities.	Length.	Surface.	Capacity.	Weight.
1000	Kilo-mètre	...	Kilo-litre	Kilo-gramme
100	Hecto-mètre	Hectare	Hecto-litre	Hecto-gramme
10	Déca-mètre	...	Déca-litre	Déca-gramme
1 (Units)	**METRE**	**ARE**	**LITRE**	**GRAMME**
·1	Déci-mètre	...	Déci-litre	Déci-gramme
·01	Centi-mètre	Centiare	Centi-litre	Centi-gramme
·001	Milli-mètre	...	Milli-litre	Milli-gramme

When the Metric method is exclusively adopted in Great Britain, these Units and Table, comprising the entire System of Weights and Measures, represent all that will be essential to be learnt in lieu of the numerous and complicated Tables hitherto in use. Adopting the style of elementary books on arithmetic, the Table may be expanded thus:—

10 milligrammes make 1 centigramme; 10 centigrammes make 1 décigramme; 10 décigrammes make one gramme; 10 grammes make 1 décagramme, or dekagramme; 10 décagrammes make 1 hectogramme; 10 hectogrammes make 1 kilogramme; 10 millilitres make 1 centilitre, etc.; 10 millimètres make 1 centimètre, etc.

Abbreviations.—Métre = *m*, décimètre = *dm*, centimètre = *cm*, millimètre = *mm*, kilomètre = *km*. Square mètre = m^2, cubic mètre = m^3, and so on. Litre = *l*, décilitre = *dl*, etc. Kilogramme = *kg*, dekagramme = *dkg*, gramme = *g*, décigramme = *dg*, centigramme = *cg*, and milligramme = *mg*.

The following approximate British equivalents of metrical units should be committed to memory:—

1 Mètre = 3 feet 3 inches and 3 eighths.
1 Are = a square whose side is 11 yards.
1 Litre = 1¾ pint.
1 Gramme = 15½ grains.
The Kilomètre is equal to 1,100 yards.
The Hectare = 2½ acres nearly.
The Metric Ton of 1,000 Kilogrammes = 19 cwt. 2 qrs. 20 lbs. 10 oz.
The Kilogramme = 2 lbs. 3¼ oz. nearly.

For *exact* equivalents, in many forms, see pp. 722 and 723. A litre of water at 39° F. weighs 15,432 grains; at 50° F., 15,429 grains; at 60° F. it weighs 15,418 grains; at 70° F., 15,403 grains; and at 80° F., 15,383 grains (Pile). (The word *gramme* is sometimes, unfortunately, written *gram*, which too closely resembles the word *grain*.)

Decimal Coinage.—In most countries where the metric system of weights and measures is employed, a decimal division of coins is also adopted. This course, conjoined with the ordinary decimal method of enumerating, which fortunately is in universal use, renders calculations of all kinds most simple,—easy to an extent which cannot be conceived in countries like England, where the operations of weighing, measuring, paying, and counting have only the most absurdly intricate relations to each other.

The General Council under whose authority the British Pharmacopœia is issued encourages medical practitioners and pharmacists in the adoption of the metric system, and gives the annexed statement of metric weights and measures.

The following Tables, from the British Pharmacopœia, and from the Diary of Messrs. De La Rue, will be found useful for reference:—

WEIGHTS AND MEASURES OF THE METRICAL SYSTEM.

WEIGHTS.

1 Milligramme	= the thousandth part of one grm. or	0·001 grm.
1 Centigramme	= the hundredth ,,	0·01 ,,
1 Décigramme	= the tenth ,,	0·1 ,,
1 Gramme	= weight of a cubic centimètre of water at 4° C.	1·0 ,,
1 Décagramme	= ten grammes	10·0 ,,
1 Hectogramme	= one hundred grammes	100·0 ,,
1 Kilogramme	= one thousand grammes	1000·0 (1 kilo.)

MEASURES OF CAPACITY.

1 Millilitre	= 1	cub. centim.	or the mea. of	1	gramme	of water.
1 Centilitre	= 10	,,	,,	10	,,	,,
1 Décilitre	= 100	,,	,,	100	,,	,,
1 Litre	=1000	,,	,,	1000	,,	(1 kilo).

MEASURES OF LENGTH.

1 Millimètre	= the thousandth	part of one mètre	or 0·001	mètre.
1 Centimètre	= the hundredth	,, ,,	0·01	,,
1 Décimètre	= the tenth	,, ,,	0·1	,,

1 Mètre = the ten-millionth part of a quarter of the meridian of the earth.

WEIGHTS AND MEASURES OF THE BRITISH PHARMACOPŒIA OF 1885.

WEIGHTS.

1 Grain	gr.			
1 Ounce	oz.		=	437·5 grains.
1 Pound	lb.	= 16 ounces	=	7000·0 ,,

MEASURES OF CAPACITY.

1 Minim	min.		
1 Fluid Drachm	fl. drm.	=	60 minims.
1 Fluid Ounce	fl. oz.	=	8 fluid drachms.
1 Pint	O.	=	20 fluid ounces.
1 Gallon	C.	=	8 Pints.

MEASURES OF LENGTH.

1 inch
12 ,, = 1 foot.
36 ,, = 3 feet = 1 yard.

(1 cubic inch of distilled water at 62° F. and 30 inch Barom. = 252·458 grains.)

RELATION OF MEASURES TO WEIGHTS.

1 Minim is the measure of		0·9114583	grain of water.
1 Fluid Drachm ,,		54·6875	grains of water.
1 Fluid Ounce ,,	1 ounce or	437·5	,,
1 Pint ,,	1·25 pound, or	8750·0	,,
1 Gallon ,,	10 pounds, or	70,000·0	,,

(Gtt. = *guttæ, drops*. The term "drop" indicates a quantity which is indefinite, and should only be used when approximativeness is alone desired.)

METRICAL MEASURES OF LENGTH.

	In English inches.	In English feet =12 inches.	In English yards =3 feet.	In English fathoms =6 feet.	In English miles =1760 yards.
Millimètre	0·03937	0·003281	0·0010936	0·0005468	0·0000006
Centimètre	0·39371	0·032809	0·0109363	0·0054682	0·0000062
Décimètre	3·93708	0·328090	0·1093633	0·0546816	0·0000621
Mètre	39·37079	3·280899	1·0936331	0·5468165	0·0006214
Décamètre	393·70790	32·808992	10·9363306	5·4681653	0·0062138
Hectomètre	3937·07900	328·089917	109·3633056	54·6816528	0·0621382
Kilomètre	39370·79000	3280·899167	1093·6330556	546·8165278	0·6213824
Myriomètre	393707·90000	32808·991667	10936·3305556	5468·1652778	6·2138242

1 inch = 2·539954 centimètres.
1 foot = 3·0479449 décimètres.
1 yard = 0·9143835 mètre.
1 mile = 1·6093149 kilomètre.

METRICAL MEASURES OF SURFACE.

	In English square feet.	In English sq. yds. =9 square feet.	In English poles= 272·25 square feet.	In English roods= 10890 square feet.	In English acres =43560 sq. feet.
Centiare, or square mètre . .	10·764299	1·196033	0·0395383	0·0009885	0·0002471
Are, or 100 square mètres . .	1076·429934	119·603326	3·9538290	0·0988457	0·0247114
Hectare, or 10,000 sq. mètres	107642·993418	11960·332602	395·3828959	9·8845724	2·4711431

1 square inch = 6·4513669 square centimètres.
1 square foot = 9·2899683 square décimètres.
1 square yard = 0·83609715 square mètre or centiare.
1 acre = 0·40467102 hectare.
1 square mile = 2·58989451 square kilomètres.

METRICAL MEASURES OF CAPACITY.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gallons = 2218·19072 cubic inches.
Millilitre, or cubic centimètre	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 cu. centimètres	0·61027	0·000353	0·01761	0·0022010	0·0002751
Décilitre, or 100 cu. centimètres	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or cubic décimètre . .	61·02705	0·035317	1·76077	0·2200967	0·0275121
Décalitre, or centistère . . .	610·27052	0·353166	17·60773	2·2009668	0·2751208
Hectolitre, or décistère . . .	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or stère, or cu. mètre	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myriolitre, or décastère . . .	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres. 1 cubic foot = 28·315312 cubic décimètres. 1 gallon = 4·535926 litres.

METRICAL MEASURES OF WEIGHT.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 112 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligramme	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Décigramme	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	**15·43235**	0·032151	0·0022046	0·0000197	0·0000010
Décagramme	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriogramme	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 gramme. 1 troy oz. = 31·103496 grams. 1 lb. avd. = 0·453593 kilogr. 1 cwt. = 50·802377 kilogrs.

QUESTIONS AND EXERCISES.

Mention some advantages of decimal weights and measures.—What is the name of the chief unit of the metric decimal system of weights and measures?—Mention the names of the metric units of surface, capacity, and weight, and state how they are derived from the unit of length.—How are multiples of metric units indicated?—State the designations of submultiples of metric units.—How many mètres are there in a kilomètre?—How many millimètres in a mètre?—How many grammes in 5 kilogrammes?—How many milligrammes in 13½ grammes?—In 1893 centigrammes how many grammes?—In a mètre measure 5 centimètres wide and 1 centimètre thick, how many cubic centimètres?—How many litres are contained in a cubic mètre of any liquid?—State the British equivalent of the mètre.—How many square yards in an are?—How many fluid ounces in a litre?—How many ounces in a kilogramme?—Give the relation of a metric ton (1,000 kilos.) to a British ton.—How many grains are there in 1 British ton?—How many ounces in 1 ton?—How many grains of water in 1 fluid drachm?–How many minims in 1 pint?—How many grains in one pint of water?—Whence is the British unit of length derived?

Specific Weight, or Specific Gravity.

The *specific* weight of a substance is its weight in comparison with the weights of similar bulks of other substances. This comparative heaviness of *solids and liquids* is conventionally expressed in relation to water: they are considered as being lighter or heavier than water. Thus, water being regarded as unity = 1, the relative weight, or specific weight, of ether is represented by the figures ·720 (it is nearly three-fourths, ·750, the weight of water), oil of vitriol by 1·843 (it is nearly twice, 2·000, as heavy as water). The specific weight of substances is, moreover, the weight of similar volumes *at sixty degrees* (60° F.); for the weight of a definite volume of any substance will vary according to temperature, becoming heavier when cooled and lighter when heated, different bodies (gases excepted) differing in their rate of contraction and expansion. While, then, specific weight or, conventionally, *specific gravity* is, truly, the comparative weight of equal bulks, the numbers which, in Great Britain, commonly represent specific gravities are the comparative weights of equal bulks at 60° F., water being taken as unity.* The standard of comparison for gases was formerly air, but is now usually hydrogen.

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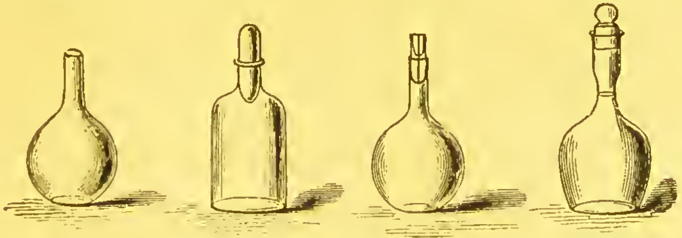
* The true weight of a body is its weight in air plus the weight of an equal bulk of air and minus the weight of a bulk of air equal to the bulk of the brass or other weights employed; or, in other words, its weight

SPECIFIC GRAVITY OF LIQUIDS.

Procure any small bottle holding from 100 to 1,000 grains (fig. 67), and having a narrow neck; counterpoise it in a delicate balance; fill it to about half-way up the neck with pure distilled water having a temperature of 60° F.; ascertain the weight of the water, and, for convenience, add or subtract a drop or two, so that the weight shall be a round number of grains; mark the neck by a diamond or file-point at the part cut by the lower edge of the curved surface of the water.

Fig. 67. *Fig.* 68. *Fig.* 69. *Fig.* 70.



SPECIFIC-GRAVITY BOTTLES.

Consecutively fill up the bottle to the neck-mark with several other liquids, cooled or warmed to 60° F., first rinsing out the bottle once or twice with a small quantity of each liquid, and note the weights; the respective figures will represent the relative weights of equal bulks of the liquids. If the capacity of the bottle is 10, 100, or 1,000 grains, the resulting weights will, without calculation, show the specific gravities of the liquids; if any other number, a proportional sum must be worked out to ascertain the weight of the liquids as compared with 1 (or 1·000) of water. Bottles conveniently adjusted to contain 250, 500, or 1,000 grains, or 100 or 50 grammes of water, when filled to the top of their perforated stopper (fig. 69), and other forms of the instrument (figs. 68

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in vacuo, uninfluenced by the buoyancy of the air; but such a correction of the weight of a body is seldom necessary, or, indeed, desirable. *Density* is sometimes improperly regarded as synonymous with *specific gravity*. It is true that the density of a body is in exact proportion to its specific gravity; but the former is more correctly the comparative bulk of equal weights, while specific gravity is the comparative weight of equal bulks.

and 70), are sold by all chemical-apparatus makers. Figure 70 is that of a bottle extremely useful in ascertaining the specific gravities of very volatile liquids.

Verify some of the following stated specific gravities of official liquids:—

Acid, acetic	1·044
,, ,, diluted	1·006
,, ,, glacial	1·058
,, carbolic	1·060 to 1·066
,, hydrochloric	1·160
,, ,, diluted	1·052
,, hydrocyanic	0·997
,, nitric	1·420
,, ,, diluted	1·101
,, nitro-hydrochloric	1·070
,, phosphoric, diluted	1·080
,, sulphuric	1·843
,, ,, aromatic	0·911
,, ,, diluted	1·094
,, sulphurous, solution of	1·025
Alcohol, absolute (real)	0·7935
,, ,, (official)	0·797 to 0·800
,, (rectified spirit, 84 per cent.)	0·838
,, (proof spirit, 49 per cent.)	0·920
,, amylic	0·818
Ammonia, aromatic spirit of	0·896
,, solution of	0·959
,, strong solution of	0·891
Antimony, solution of chloride of	1·470
Arsenic, hydrochloric solution of	1·010
Arsenical solution (*Liquor Arsenicalis*)	1·010
Benzol	0·850
Bismuth and ammonia, solution of citrate of	1·070
Bromine	2·970 to 3·140
Chlorine, solution of	1·003
Chloroform	1·490
,, spirit of	0·871
Creasote	1·071
Ether	0·735
,, pure	0·720
,, spirit of nitrous	0·840 to 0·845
Glycerine	1·250
Iron, solution of acetate of	1·031
,, ,, of dialysed	1·047
,, ,, of perchloride of	1·110
,, ,, of pernitrate of	1·107
,, ,, of persulphate of	1·441
,, strong solution of acetate of	1·127
,, ,, ,, of perchloride of	1·420

Lead, solution of subacetate of		1·275
Lime, saccharated solution of		1·052
,, solution of chlorinated		1·055
Mercury (at 0° C. = 32° F.)		13·596
,, (at 15·55° C. = 60° F.)		13·560
,, acid solution of nitrate of	(about)	2·000
Oil of eucalyptus	(about)	0·900
,, mustard		1·015
,, sandal wood	(about)	0·960
Potash, solution of		1·058
Soda, ,,		1·047
,, ,, chlorinated		1·054
Squill, oxymel of		1·320
Syrup		1·330
,, of buckthorn		1·320
,, of chloral		1·320
,, of hemidesmus		1·335
,, of iodide of iron		1·385
,, of lemons		1·340
,, of mulberries		1·330
,, of orange-flower		1·330
,, of ,, peel	(about)	1·282
,, of phosphate of iron	(about)	1·305
,, of poppies		1·330
,, of red poppy		1·330
,, of ,, roses		1·335
,, of rhubarb	(about)	1·310
,, of senna		1·310
,, of squill	(about)	1·345
,, of tolu		1·330
Treacle	(about)	1·400

Hydrometers, formerly termed *areometers.*—The specific gravity of liquids may be ascertained, without scales and weights, by means of an *hydrometer*—an instrument usually of glass, having a graduated stem and a bulb or bulbs at the lower part. The specific gravity of a liquid is indicated by the depth to which the hydrometer sinks in the liquid, the zero of the scale marking the depth to which it sinks in pure water. Hydrometers constructed for special purposes are known under the names of saccharometer, lactometer, elæometer, urinometer, alcoholometer. Hydrometers require a considerable quantity of liquid fairly to float them; and specific gravities observed with them are less delicate and trustworthy than those obtained by the balance, nevertheless they are exceedingly useful for many practical purposes where the employment of a delicate balance would be inadmissible.

Specific Gravity of Solids in Mass.

Weigh a piece (50 to 250 grains) of any solid substance heavier than water in the usual manner. Then weigh it in water, by suspending it from a shortened balance-pan by a fine thread or hair and immersing in a vessel of water (fig. 71). The buoyant properties of the water will cause the solid apparently to lose weight; *this loss in weight is the exact weight of an equal bulk of water.* The weight of the substance and the weight of an equal bulk of water being thus ascertained, a proportional sum shows the relative weight of the substance to 1·000 of water. To express the same thing by rule, divide the weight in air by the loss of weight in water, the resulting number is the specific gravity in relation to 1 part of water, the conventional standard of comparison.

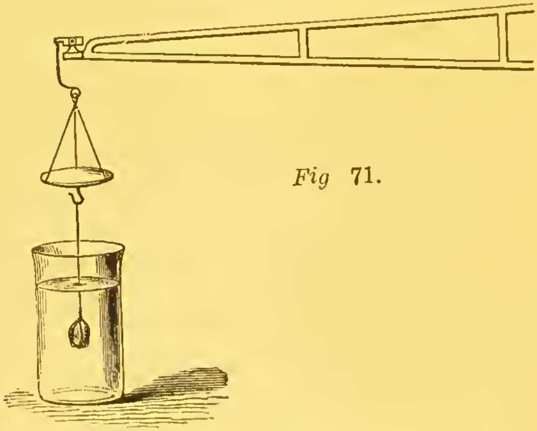

Fig 71.

WEIGHING A SOLID IN WATER.

Verify some of the following specific gravities :—

Aluminium	2·56
Antimony	6·71
Bismuth	9·83
Coins, English, gold	17·69
,, ,, silver	10·30
,, ,, bronze	8·70
Copper	8·95
Gold	19·34

Iron	7·84
Lead	11·36
Magnesium	1·74
Marble	2·70
Phosphorus	1 77
Platinum	21·53
Silver	10·53
Sulphur	2·05
Tin	7·29
Zinc	7·14

Specific gravities of solid substances should be taken in water having a temperature of about 60° F. The body should be immersed about half an inch below the surface of the water; adhering air-bubbles must be carefully removed; the body must be quite insoluble in water.

(For a table of the specific gravities of a large number of fatty and resinoid substances, *see* the *Pharmaceutical Journal* for Oct. 11, 1879.)

SPECIFIC GRAVITY OF SOLIDS IN POWDER OR SMALL FRAGMENTS.

Weigh the particles; place them in a counterpoised specific-gravity bottle of known capacity, and fill up with water, taking care that the substance is thoroughly wetted; again weigh. From the combined weights of water and substance subtract the amount due to the substance: the residue is the weight of the water. Subtract this weight of water from the quantity which the bottle normally contains: the residue is the amount of water displaced by the substance. Having thus obtained the weights of equal bulks of water and substance, a proportional sum shows the relation of the weight of the substance to 1 part of water, *i.e.* the specific gravity.

Or, suspend a cup, short glass tube, or bucket from a shortened balance-pan; immerse in water; counterpoise; place the weighed powder in the cup, and proceed as directed for taking the specific gravity of a solid in mass.

This operation may be conducted on fragments of any of the substances the specific gravities of which are given in the foregoing Table, or on the powdered piece of marble the specific gravity of which has been taken in mass. The specific gravity of one piece of glass, first in mass then in powder, may be ascertained; the result should be identical. The specific gravity of shot is about 11·350; sand, 2·600; mercury, 13·56.

Specific Gravity of Solids Soluble in Water.

Weigh a piece of sugar or other substance soluble in water: then suspend it from a balance in the usual manner, and weigh it in turpentine, benzol, or petroleum, the specific gravity of which is known or has been previously determined; the loss in weight is the weight of an equal bulk of the turpentine. Ascertain the weight of an equal bulk of water by calculation:—

Sp. gr. of turpentine : sp. gr. of water :: observed bulk of turp. : equal bulk of water.

The exact weights of equal bulks of sugar and water being obtained, the weight of a bulk of sugar corresponding to 1·000 of water is shown by a proportional sum; in other words, divide the weight of sugar by that of the equal bulk of water, the quotient is the specific gravity of sugar. The stated specific gravity of sugar ranges from 1·590 to 1·607.

Specific Gravity of Solids Lighter than Water.

This is obtained in a manner similar to that for solids heavier than water; but the light body is sunk by help of a piece of heavy metal, the bulk of water which the latter displaces being deducted from the bulk displaced by both; the remainder is the weight of a bulk of water equal to the bulk of the light body. For instance, a piece of wood weighing 12 grammes (or grains—for it is assumed that the student works equally well with metric as with imperial weights—is tied to a piece of metal weighing 22 grammes, the loss of weight of the metal in water previously having been found to be 3 grammes. The two, weighing 34 grammes, are now immersed, and the loss in weight found to be 26 grammes. But of this loss 3 grammes have been proved to be due to the buoyant action of the water on the metal; the remaining

23, therefore, represent the same effect on the wood; 23 and 12, therefore, represent the weights of equal bulks of water and wood. As 23 are to 12, so is 1 to ·5217. Or, shortly, as before, divide the weight in air by the weight of an equal bulk of water; ·5217 is the specific gravity of the wood. Another specimen of wood may be found to be three-fourths (·750) the weight of water, and others heavier. Cork varies from ·100 to ·300.

The specific gravity of a very minute quantity of a heavy or light substance may be ascertained by noting the specific gravity of a fluid in which it, being insoluble, neither sinks nor swims; or by immersing it in a weighed piece of paraffin whose specific gravity is known, noting the specific gravity of the whole, and deducting the influence of the paraffin.

SPECIFIC GRAVITY OF GASES.

This operation is similar to that for liquids. A globe exhausted of air and holding from 1 to 4 litres (or quarts) is suspended from the arm of a balance, and counterpoised by a similar flask. Gases are introduced in succession and their weights noted. A proportional sum shows their specific gravity in relation to air or hydrogen, whichever be taken as a standard.

Correction of the Volume of Gases for Pressure.—The height of the barometer at the time of manipulation is noted. Remembering that "the bulk of a gas is inversely as the pressure to which it is subjected" (Boyle and Mariotte), a simple calculation shows the volume which the gas would occupy at 760 millimètres (or 29·992 inches), the standard pressure (30 inches is sometimes adopted as the standard in England).* Thus 40 volumes of a gas at 740 millims. pressure are reduced to 39 when the pressure becomes 760 millimètres (or 90 vols. at 29 ins. barom. become 87 vols. at 30 inches).

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* In France the conventional standard height of the barometer is 760 millimètres at 0° C. (32° F.); in England it is 30 inches, the temperature being 60° F. 760 millims. is equivalent to 28·922 inches; but the expansion of the metal between 32° F. and 60° F. increases the length of the column to 30·005 inches. The standards are therefore almost identical, difference in true length being counterbalanced by the temperature at which the length is observed.

Correction of the Volume of Gases for Temperature.—This is done in order to ascertain what volume the gas would occupy at 0° C. (32 F.) or 15·5 C. (60° F.), according to the standard taken. Gases are equally affected by equal variations in temperature (Charles). They expand about 0·3665 * per cent. ($\frac{1}{273}$) of their volume *at the freezing-point of water* for every C. degree (0·2036, or $\frac{1}{491}$ for every F. degree) (Regnault). Thus 8 volumes of gas at 0° C. will become 8·293 at 10° C.; for if 100 become 103·665 on being increased in temperature 10° C., 8 will become 8·293 (or if 100 become 102·036 on being increased 10° F., 8 will become 8·1629).

Vapour-density.—Vapours are those gases which condense to liquids at common temperatures. By the density of a vapour is meant its specific gravity. The density of a vapour is the ratio of any given volume to a similar volume of air or hydrogen at the same temperature and pressure. But, for convenience of comparison, this experimental specific gravity is referred, by calculation as just described for permanent gases, to a temperature of 0° C., and 760 millimètres barom. A teaspoonful or so of liquid is placed in a weighed flask of about the capacity of a common tumbler and having a capillary neck: the flask is heated in an oil-bath to a temperature considerably above the boiling-point of the liquid; at the moment vapour ceases to escape, the neck is sealed by a blowpipe flame, and the temperature of the bath noted; the flask is then removed, cooled, cleaned, and weighed; the height of the barometer is also taken. The neck of the flask is next broken off beneath the surface of water (or of mercury), which rushes in and fills it, and again weighed, by which its capacity in cub. centims. is found. From these data the volume of vapour yielded by a given weight of liquid is ascertained by a few obvious calculations. The capacity of the globe having been ascertained, the weight of an equal bulk of air † is obtained by a rule-of-three sum. This weight of air is deducted from the original weight of the flask, which gives the true weight of the glass. The weight of the glass is next subtracted from the weight of the flask and contained vapour (now condensed), which gives the weight of material used in the experiment. The volume which this weight of material occupied at the time of experiment is next corrected for temperature (to 0° C.) and pressure (760 millimètres) in the manner just described. The weight of a similar volume of hydrogen is next found.* The weights of equal volumes of hydrogen and vapour being thus determined, the amount of vapour corresponding to 1 of hydrogen (the specific gravity or vapour-density) is shown by a short calculation. This process of finding the weight of a given volume of vapour is by Dumas. Gay-Lussac's consists in determining the volume of a given weight: it has been improved by Hofmann. An easy and excellent method by V. and C. Meyer consists, like that of Gay-Lussac, in determining the volume of the vapour of a given weight of a fluid or solid, but differs in the volume of the vapour being ascertained from an equal volume of air which the vapour is made to displace. (For a detailed description of this method, and a drawing of the apparatus, *see Pharmaceutical Journal*, May 17, 1879.)

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* Corrected for the difference between the mercurial and air-thermometers, the coefficient of expansion of air is 0·003656 (Miller). The coefficient of expansion of different gases varies very slightly, being somewhat higher for the more liquefiable gases.

† 1 cubic centimètre of air at 0° C. and 760 millims. weighs 0·001293 gramme.

Experiment shows that the specific gravities of many gases and vapours on the hydrogen scale and the proportions in which they combine by weight are identical. Thus chlorine is 35·5 times as heavy as hydrogen, and 35·5 parts unite with 1 of hydrogen to form hydrochloric acid gas. Hence if the specific gravity of a gas or vapour is known, its combining-proportion may be predicated with reasonable certainty, and *vice versâ*. In applying this rule to gaseous or vaporous compounds, attention must be paid to the extent to which their constituent gases contract at the moment of combination or expand at the moment of decomposition.

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* I litre (1000 cub. centims.) of hydrogen at 0° C. and 760 millimètres (the barometer being at 0° C.) weighs 0·0896 gramme—a quantity sometimes termed a *crith* (from *κριθὴ*, *krithē*, a barley-corn—figuratively, a small weight); thus a litre of oxygen weighs 16 criths, chlorine, 35·5 criths, etc. 100 cubic inches of hydrogen at 32° F. weigh 2·265 grains; at 60° F. 2·143 grains (the barometer being 30 ins. at 60° F. in both cases). 100 cubic inches of air at 32° F. weigh 32·698 grains; at 60° F., 30·935 (barom. 30 ins. at 60° F.). 1 cubic inch of water weighs 252·458 grains (Chaney, 252·279) at 62° F., and 30 in. bar. 1 gallon of water contains 277¼ (277·274 at 62° F.) cubic ins. 1 cubic foot contains about 6¼ gallons.

Thus steam is found to be composed of two volumes of hydrogen and one of oxygen, the three volumes of constituents condensing to two at the moment of combination. Hence steam may be expected to be nine times as heavy as hydrogen, which experiment confirms.

These relations may be so expressed as to include both elementary and compound gases and vapours, thus: *molecular weights and specific weights are identical.* Molecular weights represent two volumes of a gas: specific gravity conventionally represents the relative weight of a gas compared with *one* volume of hydrogen or air; hence the specific gravity of a gas or vapour on the H scale is found by calculation on simply dividing the molecular weight by 2; on the air scale by dividing the hydrogen numbers by 14·44. For example:—

Name.	Molecular formula.	Molecular weight.	Specific gravity.		
			H=2.	H=1.	Air=1.
Hydrogen	H_2	2	2	1	·069
Chlorine	Cl_2	71	71	35·5	2·460
Oxygen	O_2	32	32	16	1·108
Nitrogen	N_2	28	28	14	·970
Steam	H_2O	18	18	9	·624
Ammonia gas . . .	NH_3	17	17	8·5	·589
Carbonic acid gas . .	CO_2	44	44	22	1·524
Alcohol (vapour) . .	C_2H_6O	46	46	23	1·593
Air	—	—	28·88	14·44	1·000

In other words, it follows, as an arithmetical necessity, that if the specific gravities of gases or vapours have been rightly determined and the molecular weights of those gases and vapours have been quite accurately ascertained, the product of the division of the figures showing the molecular weights by the figures showing the specific gravities will be quotients that will always be the same number. If the specific gravity be in relation to two volumes of hydrogen the quotient will in all cases be the figure 1, or, obviously, the figures for specific gravity and molecular weight will be identical. If the specific gravity figure be in relation to one volume of hydrogen, the quotient will be the figure 2; if in relation to air, the quotient will be 28·88 (air being 14·44 times heavier than hydrogen). By multiplying 28·88 by the specific gravity on the air-scale the experimental figure obtained for molecular weight can be checked. So by dividing the molecular weight by 28·88 the specific gravity on the air-scale can be checked. Once more, divide the molecular weight by the specific gravity on the air-scale and the quotient will not be far from 28·88 if the two figures have been ascertained with all attainable experimental exactitude.

The foregoing columns of specific gravities closely correspond with those obtained by actual experiment. The specific gravity of any gas or vapour may therefore be calculated if the following data are at hand:—(*a*) formula, (*b*) atomic weight of constituent elements; these give the molecular weight, and *the molecular weight divided by* 2 *is the specific gravity* on the hydrogen scale. Specific gravity on the air-scale is then deducible, if (*c*) the specific gravity of air (14·44) in relation to hydrogen be remembered. The absolute weight of any volume of a gas or vapour on the metric system is then obtainable if (*d*) the weight of a litre of hydrogen (0·0896 gramme) be known, or on the English plan by remembering (*e*) that 100 cubic inches of hydrogen at 60° F. weigh 2·143 grains (100 cubic inches of air at 60° F. weigh 30·935 grains).

In confirmation of these statements regarding the mutual relation of specific gravity and atomic weight, a remarkable fact may be mentioned. Regnault several years ago found the weight of 1 litre of hydrogen and oxygen to be respectively ·089578 and 1·429802 gramme. The latter number divided by the former gives 15·96 as the specific gravity of oxygen. Stas, in recent experimental researches on combining-proportion, finds the atomic weight of oxygen to be, not 16, but 15·96.

Exceptions to the law occur in a few compounds and in arsenium and phosphorus, whose vapour densities are twice that indicated by the rule. Possibly in these cases the temperature employed is insufficient to dissociate an unusually complex molecule into molecules of usual complexity. As regards compounds, and, possibly, as regards those elements in which the observed density is only half that indicated by this rule, heat may, and in some cases probably does, produce molecular *dissociation* (*thermolysis*) into free atoms (uniatomic molecules) or into less complex molecules. *See* page 221.

Relation of the Specific Heat of Elements to their Atomic Weights.—Reference may here appropriately be made to a physical fact of great importance as regards molocular and atomic weights. In the earlier pages of this Manual it was stated that elements do not combine chemically in haphazard proportions, but in fixed weights; and abundant evidence of the truth of the statement has already been afforded, and will also be found in this section on quantitative analysis. Secondly, it has been shown that elements do not combine in haphazard proportions by volume, but in certain constant bulks; and the weights of these bulks have been found to be identical with the combining weights themselves. Thirdly (this is the point to which attention is now drawn), if equal amounts of heat be given to the elements in the solid state (that is, to solid elements or to solid compounds of volatile elements), and the quantity of the element be increased or diminished until each is thus heated through an equal number of degrees, it will be found that the different weights of elements required are (in relation to a common standard) identical with the combining weights of the elements, and with the weights of the combining volumes of the elements. Thus, where 108 parts of silver would be employed, 207 of lead would be necessary.[*] Hence, in the determination of (*a*) combining-proportion, (*b*) specific gravity in gaseous state, and (c) specific heat, three distinct methods of ascertaining atomic weight are available. In cases where one method is inapplicable recourse is had to either or, if practicable, both of the others, and thus the trustworthiness of observations and generalizations placed more or less beyond question. The specific heat of a solid element is the same in the free as in the combined condition; therefore the specific heat of a molecule is the sum of the specific heats of its constituent atoms. From the specific heat of a solid compound of a volatile element (chlorine, for example) can thus be calculated the specific heat of an element in the solid state, even though the free element cannot itself be solidified. For the processes by which experimentally to determine specific heat, the reader is referred to books on physics.

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[*] Obviously, if equal weights of silver and lead were heated through an equal number of degrees, the silver would absorb nearly twice as much heat as the lead. In fact, as regards all the solid elements, "specific heats and atomic weights are inversely proportional." This law was discovered by Dulong and Petit. It follows that the product of the multiplication of the figures representing the specific heat of an element with the figures representing its atomic weight is in the case of nearly every such element the same number, namely 6, more or less, according to the care with which the experiments have been conducted. Some exceptions to the law have disappeared when the experiments have been conducted at a sufficiently high temperature.

There is equivalency also between *electrical* and chemical action. The amount of electricity which passed through an iodide, would, by the resulting *electrolysis* (electric *loosing*, from λύω, *luo*, to decompose) set free 127 parts of iodine would set free 80 parts of bromine.

Again, Raoult reflecting that the degree to which the solidifying point of a fluid is affected by a dissolved substance is dependent on the molecular weight of that substance, has shown that determinations of such degrees point to molecular weights. (Further researches in this direction will probably throw much light on the nature of the phenomena of *solution.*) Optical activity and molecular weight would also seem to be inter-dependent.

QUESTIONS AND EXERCISES.

Define specific weight, or, as it is commonly termed, specific gravity.—In speaking of light and heavy bodies specifically, what standard of comparison is conventionally employed?—How are specific gravities expressed in figures?—Why should specific gravities be taken at one constant temperature?—How does the buoyancy of air affect the real weight of any material?—Describe the difference between density and specific gravity. —Give a direct method for taking the specific gravity of liquids.—A certain bottle holds 150 parts, by weight, of water, or 135·7 of spirit of wine; show that the specific gravity of the latter is 0·9046.—An imperial fluid ounce of a liquid weighs 366½ grains; prove that its specific gravity is 0·838.—Equal volumes of benzol and glycerine weigh 34 and 49 parts respectively, and the specific gravity of the benzol is 0·850; show that the specific gravity of the glycerine is 1·225.—Explain the process employed in taking the specific gravity of solid substances in mass and in powder.—State the method by which the specific gravity of a light body, such as cork, is obtained.—What modifications of the usual method are necessary in ascertaining the specific gravity of substances soluble in water?—How is the specific gravity of gases determined?—By what law can the volume of a gas, at any required pressure, be deduced from its observed volume at another pressure?—To what extent will 78 volumes of a gas at 29·3 inches barom. alter in bulk when the pressure is 30·2 inches?—Write a short account of the means by which the volumes of gases are corrected for temperature.—At the temperature of 15° C. 40 volumes (litres, pints, ounces, cubic feet, or other quantity) of a gas are measured. To what extent will this amount of gas contract on being cooled to the freezing-point of water (0° C.)? *Answer:* As 1 vol. of any gas *at zero* expands or contracts ·003665 of a vol. for each rise or fall of 1° C., 1 vol. at 0° C. if heated to 15° C. will become increased by ·054975 (that is, ·003665 multiplied by 15), 1 vol. will expand to 1·054975. Conversely 1·054975 vol. will contract to 1 vol. if cooled from 15° C. to 0° C. And if 1·054975 becomes 1 in cooling through 15° C., 40 vols. will (as found by rule of three) contract to 37·916.—10 litres of oxygen are measured off at 14° F. Required the volume of the gas at 15° C. *Answer:* The first operation must be to reduce the temperature quoted in Fahrenheit's degrees to an equivalent value on the Centigrade scale. 14° F., is 18° below 32° F., the freezing-point of water; and a range of 9° on the Fahrenheit scale is equal to a range of 5° on the Centigrade scale, so that the temperature at which the oxygen is measured off is −10° C. The rise of temperature up to 0° expands the gas in such proportion that its volume at 0° is to its volume at −10° as 1 is to $1-0{\cdot}03665$, *i.e.* as 1 to 0·96335. The further rise of temperature from 0° C. to 15° expands the gas in the proportion of 1 to $1+15\times0{\cdot}003665$, *i.e.* 1 to 1·054975. The total rise of temperature therefore expands the gas in the proportion of 0·96335 to 1·054975.

$$0{\cdot}96335 : 1{\cdot}054975 :: 10 : x;$$

$$\therefore x=\frac{10\times1{\cdot}054975}{0{\cdot}96335}=10{\cdot}95.$$

—230 cubic centimètres of oxygen are measured off at 14° C. and 740 millimètres mercurial pressure. Required the volume of the gas at the normal temperature and pressure (0° C. and 760 millimètres. *Answer:* Let the reduction for change of temperature be made first. The proportion—

$$1+(14\times0{\cdot}003665) : 1 :: 230 : x$$

gives

$$x=\frac{230}{1{\cdot}05131}=218{\cdot}774.$$

To reduce this volume at 740 millimètres pressure to the volume corresponding to the pressure of 760 millimètres, we have the proportion—

$$760 : 740 :: 218{\cdot}77 : x;$$

whence

$$x=\frac{740\times218{\cdot}77}{760}=213{\cdot}02.$$

—A litre of oxygen is confined in a glass flask at 10° C. by the atmospheric pressure, added to that of a column of mercury 60 millimètres high. The flask must be heated to 300° C. without any increase of volume taking place in the oxygen. How high must the column of mercury then be which presses on the gas, supposing the atmospheric pressure to remain constant at 760 millimètres? *Answer:* The oxygen is given at 10° C. and 820 millimètres pressure. If the pressure remained constant, the rise of temperature from 10° C. to 300° C. would expand the gas in such proportion that 1·03665 volume would expand to 2·0995 volumes. In order to prevent any expansion the pressure must be increased in the same proportion, whence

$$1{\cdot}03665 : 2{\cdot}0995 :: 820 : x;$$

$$\therefore x=\frac{820\times2{\cdot}0995}{1{\cdot}03665}=1660{\cdot}6.$$

From this total pressure the atmospheric pressure of 760 millimètres has to be deducted, leaving 900·6 millimètres as the height of the required mercurial column.—A litre of oxygen is required of the density of 100 at 0° C. What weight of potassic chlorate must be used for its preparation, and what total pressure must be applied to it? *Answer:* The pressure required to compress oxygen from the density of 16 to that of 100 is found by the proportion—

$$16 : 100 :: 760 : x$$

$$\therefore x = \frac{76000}{16} = 4750.$$

At the pressure of 4750 millimètres of mercury the weight of a litre of oxygen (16 grammes measure 11·2 litres at 0° C. and 760 millims. pressure) is found by the proportion—

$$760 : 4750 :: \frac{16}{11{\cdot}2} : x;$$

whence

$$x = \frac{16 \times 4750}{11{\cdot}2 \times 760} = 8{\cdot}93 \text{ grammes.}$$

The weight of chlorate required for the evolution of 8·93 grammes of oxygen is found from the proportion—

$$48 : 122{\cdot}5 :: 8{\cdot}93 : x;$$

$$\therefore x = 22{\cdot}8 \text{ grammes.}$$

—What is the volume of 12 grammes of hydrogen at 15° C.? *Answer:* One gramme of hydrogen measures 11·2 litres at 0° C., therefore 12 grammes measure $12 \times 11{\cdot}2 = 134{\cdot}4$ litres at 0°. To find their volume at 15° C. we have the proportion—

$$1 : 1 + 15 \times 0{\cdot}003665 :: 134{\cdot}4 : x;$$

whence

$$x = 134{\cdot}4 \times 1{\cdot}054975 = 141{\cdot}788 \text{ litres.}$$

(The foregoing five problems are from Williamson's "Chemistry.")

—What interest for chemists have the specific heats of substances?

VOLUMETRIC QUANTITATIVE ANALYSIS.

Preliminary Note.—Great care should be observed in selecting a *fair* sample of any bulk of material that is to be examined either by volumetric or gravimetric quantitative analysis. If the whole quantity is in separate parcels, and there is any ground for believing that the parcels differ in quality, they should, if practicable, be carefully mixed, or, technically, "bulked." Small portions should be taken from different parts of the resulting heap and well mixed in a mortar or other vessel, or, in certain cases, dissolved, and the solution well stirred or shaken. A specimen of the powder, or a portion of the solution, may then be selected for analysis.

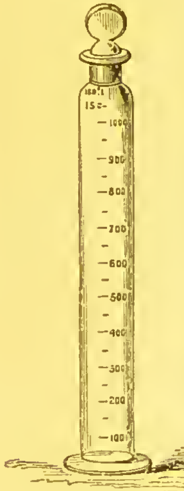
Introduction.—The operations of volumetric analysis consist (*a*) in carrying out some definite *chemical reaction*, already well known to the operator, with (*b*) *definite quantities* of substances or salts; (*c*) the exact termination of the reaction between the two salts or substances being ascertained—usually by some *chemical indicator* (litmus, starch, etc.). A portion of the substance or salt, etc., to be tested is carefully weighed. To this is gradually added the second substance or salt contained in the testing fluid, commonly termed the Standard Volumetric Solution. The usefulness, and, indeed, the preparation of this Standard Solution is founded (as already indicated on page 707) on some accurate initial gravimetric operation. A *weighed* amount of a pure salt is dissolved in a given *volume* of water. "Accurately *measured* quantities of such a Standard Volumetric Solution will obviously contain just as definite amounts of the dissolved salt as if those amounts were actually *weighed* in a balance, and as measuring occupies less time than weighing, the volumetric operations can be conducted with great economy of time, as compared with the corresponding gravimetric operations."

Normal solutions contain one molecular weight of substance, in grammes, per litre.

APPARATUS.

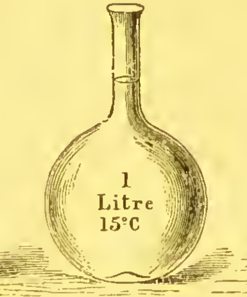
The only special vessels necessary in volumetric quantitative operations are:—1. A *litre flask* (fig. 73), which, when filled to a mark on the neck, contains at 15° C., or about 60° F., one litre (1,000 cubic centimètres, *i.e.* 1,000 grammes of water*); it serves for preparing solutions in quantities of one litre. 2. A tall cylindrical *graduated litre jar* (fig. 72) divided into 100 equal parts; it serves for the measurement and admixture of decimal or centesimal parts of one litre.

Fig. 72.



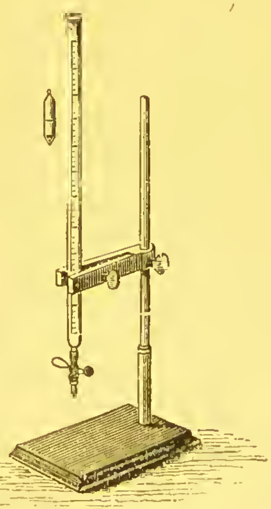
A LITRE JAR.

Fig. 73.



A LITRE FLASK.

Fig. 74.



A BURETTE, ETC.

3. A graduated tube or *burette* (fig. 74), the marked portion of which, when filled to "0," holds 100 cubic centimètres, and is divided into 100 equal parts, with subdivisions; it is used for accurately measuring small volumes of liquids.

The best form of burette is Mohr's. It consists of a glass tube, commonly about the width of a little finger and the length of an arm from the elbow, contracted at the lower extremity and graduated. The width and length of burettes, however, as well as the extent and fineness of their graduation, vary considerably. To the contracted portion is fitted a

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[*] A cubic centimètre is, strictly speaking, the volume occupied by one gramme of distilled water at its point of greatest density, namely, 4° C. Metric measurements, however, are uniformly taken at 15·55° C. (60° F.).

small piece of vulcanized caoutchouc tubing, into the other end of which a small spout made of narrow glass tube is tightly inserted. A strong wire clamp effectually prevents any liquid from passing out of the burette unless the knobs of the clamp are pressed by the finger and thumb of the operator, when a stream or drops flow at will. In place of the india-rubber tubing and clamp, a stopcock is sometimes employed; and other modes of arresting the flow of liquid may be adopted. The accurate reading of the height of a solution in the burette is a matter of great importance; it should be taken from the bottom of the curved surface of the liquid. It may be still more exactly measured by the employment of a hollow glass float or bulb (Erdmann's float, *see* fig. 74), of such a width that it can move freely in the tube without undue friction, and so adjusted in weight that it shall sink to more than half its length in any ordinary liquid. A fine line is scratched round the centre of the float; this line must always be regarded as marking the height of the fluid in the burette. In charging the burette, a solution is poured in, not until its surface is coincident with 0, but until the mark on the float is coincident with 0. Avoid accumulation of air behind the india-rubber.

ESTIMATION OF ALKALIES, ETC.

VOLUMETRIC SOLUTION OF OXALIC ACID.

(Crystallized Oxalic Acid, $H_2C_2O_4,2H_2O = 126$.)

The oxalic radical, being bivalent, and most of the metals contained in the salts which are estimated by oxalic acid being univalent, it is convenient that each litre of this solution should contain half a molecular weight in grammes of the acid ($H_2C_2O_4, 2H_2O = 126 \div 2 = 63$)—be "semidecinormal".

If pure crystallized oxalic acid be at hand, the solution is made by dissolving 63 grammes in water, and making the volume up with more water to exactly one litre.

Pure oxalic acid, however, not being easy to obtain, the solution may be made from the commercial acid by dissolving 65 to 70 grammes in enough water to make a litre of solution, and then determining the strength of this solution by titration with pure carbonate of sodium, making use of the following memoranda:—

$$\underbrace{Na_2CO_3}_{\substack{2)106 \\ \overline{53}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126 \\ \overline{63}}} = Na_2C_2O_4 + CO_2 + 3H_2O.$$

Pure anhydrous carbonate of sodium is easy to obtain, for commercial bicarbonate is usually of such purity that when a few grammes are heated to redness for a quarter of an hour, the resulting carbonate is practically free from impurity. The bicarbonate should, however, be tested, and if more than traces of chlorides and sulphates are present, these may be removed by washing a few hundred grammes, first with a saturated solution of bicarbonate of sodium, and afterwards with pure distilled water. After drying, the salt is ready for ignition.

About half a gramme of the carbonate of sodium is accurately weighed and placed in a half-pint flask, around the neck of which is tied calico or leather to protect the fingers when the heated vessel is shaken by the operator. The salt is dissolved in water to about one-third the capacity of the flask, and a few drops of the indicator, blue tincture of litmus, is added. The acid solution to be "set" or "standardized" is then poured into a burette and run therefrom into the flask until the reddened litmus indicates the presence of free acid. This will be due in the first place to carbonic acid liberated and remaining dissolved in the solution. The contents of the flask are therefore boiled for several minutes, when the blue colour will have returned. More acid is then run in until the mixture, after boiling, remains of a neutral colour, indicating that just enough acid has been added to complete the reaction expressed in the foregoing equation.

Let it be supposed that ·6 of a gramme of carbonate of sodium was taken, and that this required 11 c.c. of oxalic acid solution, how many c.c. of this solution would contain 63 grammes of oxalic acid crystals; or, what is equivalent in the reaction, how many c.c. would be required to neutralize 53 grammes of carbonate of sodium? As ·6 of a gramme of the carbonate is to 11 c.c. sol., so are 53 grammes of the carbonate to x c.c. sol., therefore $x = 972$ c.c. 972 c.c. (nearly) are equivalent to 53 grammes of carbonate of sodium, and contain 63 grammes of oxalic acid.

This oxalic solution may be used as it is or may be diluted with water, every 972 c.c. to be diluted to 1,000 c.c., so that 1,000 c.c. shall contain 63 grammes of oxalic acid.

The following official substances are tested by this solution according to the British Pharmacopœia :—

Solutions of Ammonia.—Two or three grammes of dilute, or about 1 gramme of strong solution of ammonia, is a convenient quantity to operate upon. The weighing is most conveniently accomplished by taking a small stoppered bottle containing half an ounce or so of the substance, and having ascertained its total weight, transfer about the quantity desired to the flask in which the estimation is to be conducted, and again weigh the bottle with what remains in it. The difference is the exact quantity taken. The weighing of the ammonia solution having been accomplished, water is added, to about one-third the capacity of the flask (or, better, the ammonia is added to water already in the flask), and a few drops of tincture of litmus are introduced. The titration is then conducted as described before, except that no heat is employed.

$$\underbrace{2NH_4HO}_{\substack{2)70\\ \overline{35}}} \quad + \quad \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}\,=\,\text{grammes in 1,000 c.c. of standard solution.}}} \quad = \quad (NH_4)_2C_2O_4 \quad + \quad 4H_2O.$$

$$\underbrace{2NH_3H_2O}_{\substack{2)34\\ \overline{17}}} \quad + \quad \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}\,=\,\text{grammes in 1,000 c.c. of standard solution.}}} \quad = \quad (NH_4)_2C_2O_4 \quad + \quad 4H_2O.$$

1,000 c.c. of standard solution, or its equivalent of a solution of any other strength, would, according to this reaction, neutralize 17 grammes of ammonia gas (NH_3) or 35 grammes of hydrate of ammonium (NH_4HO). If 3 grammes of ammonia solution had been taken, and it had required 15 c.c. of standard oxalic acid solution, then the amount of ammonia gas or hydrate of ammonium it contained would be seen by the following calculations :—

1000 c.c. : $17NH_3$: : 15 c.c. : x = ·255 grammes NH_3
1000 c.c. : 35 NH_4HO : : 15 c.c. : x = ·525 grammes NH_4HO

Three grammes, then, would contain ·255 grammes of the gas, or ·525 grammes of hydrate of ammonium. Or in percentage :—

3 gr. sol. : ·255 gr. NH_3 : : 100 gr. sol. : x gr. NH_3 = 8·5% NH_3
3 gr. sol. : ·525 gr. NH_4HO : : 100 gr. sol. : x gr. NH_4HO = 17·5% NH_4HO

The solution would therefore contain 8·5 per cent. of ammonia gas (NH_3) or 17·5 per cent. of hydrate of ammonium (NH_4HO). If the oxalic acid solution was not of full standard, the number of c.c. which contained 63 grammes of oxalic acid, which was, in fact, equivalent to 1,000 c.c. of standard solution, would be substituted for 1,000 c.c. in the preceding proportions.

A comparison should now be made with the requirements of the Pharmacopœia. It is useful to express results as percentage of substance of pharmacopœial strength in the material examined. Thus the British Pharmacopœia requires dilute ammonia solution to contain 10 per cent. of the gas (NH_3). The solution supposed to have been operated on contained 8·5 per cent. NH_3 ($10 : 8·5 :: 100 : x = 85$). Therefore it contains 85 per cent. of the dilute ammonia of the British Pharmacopœia.*

Strong Solution of Ammonia, B.P., contains 32 per cent. of ammonia gas (NH_3).

Note.—The calculations just described for ammonia are similar to those employed throughout volumetric analysis; they will not be repeated, therefore, in the case of every substance.

Carbonate of Ammonium.—The reactions indicated by the

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* Extremely minute quantities of ammonia—1 part in many millions of water—may be estimated volumetrically by adding excess of a colourless, strongly alkaline, solution of red iodide of mercury and iodide of potassium, "Solution of Potassio-mercuric Iodide," B.P., or "Nessler's Reagent;" then in a similar vessel, containing an equal amount of pure water with excess of the Nessler reagent, imitating the depth of yellow or reddish-yellow colour thus produced by adding an ammoniacal solution *of known strength.* The amount of ammonia thus added represents the amount in the original liquid.

The Nessler Reagent.—A litre may be made by dissolving 30 or 40 grammes of iodide of potassium in a small quantity of hot water, adding a strong hot solution of perchloride of mercury until the precipitate of mercuric iodide ceases to redissolve even by the aid of rapid stirring and heat, slightly diluting, filtering, adding a strong solution of (120 to 140 grammes of) caustic soda, or (160 to 180 grammes of) caustic potash, and diluting to one litre. A few c.c. (5 or 6 or more) of a strong solution of perchloride of mercury are finally stirred in, the whole set aside till all precipitated red iodide has deposited, and the clear liquid decanted for use. The reaction of this Nessler test with ammonia is as follows :—

$$NH_3 + 2HgI_2 + 3KHO = NHg_2I + 3KI + 3H_2O.$$

Potassio-mercuric Iodide, without alkali, is commonly known as *Mayer's Reagent*, HgI_22KI. Decinormal strength is convenient.

following equations occur between commercial carbonate of ammonium and oxalic acid :—

$$\underbrace{2N_3H_{11}C_2O_5}_{\substack{6)314\\ \overline{\;52\cdot3\;}}} + \underbrace{3(H_2C_2O_4,2H_2O)}_{\substack{6)378\\ \overline{\;63\;}}} = 3(NH_4)_2C_2O_4 + 8H_2O + 4CO_2$$

63 = grammes in 1,000 c.c. of standard solution.

About 1 gramme is a convenient quantity to operate upon. Tincture of litmus is the indicator, and the titration is conducted at a temperature just short of boiling. The estimation is not very satisfactory, because the heat employed, while scarcely sufficient to expel the carbonic acid gas, is enough to occasion loss of ammoniacal salt. Practised analysts usually add excess of the standard acid and thus fix every trace of ammonia ; then gently boil to get rid of carbonic acid gas ; bring back the liquid to neutrality by an observed volume of standard alkaline solution, and deduct an equivalent volume of acid from the quantity first added. The British Pharmacopœia requires 5·23 grammes to neutralize 100 c.c. of standard solution of oxalic acid. This corresponds to 100 per cent. of carbonate having the formula $N_3H_{11}C_2O_5$.

Spiritus Ammoniæ Aromaticus, B.P.—The *alkalinity* of the official sal volatile (*see* p. 101) should be such that "one fluid ounce [392 grains weight] requires for neutralization 558 grain-measures of the volumetric solution of oxalic acid" ; and, if the proper proportion of *carbonate* of ammonium is present, "one fluid ounce, after the addition of 330 grain-measures of the test solution of chloride of barium [1 to 10 of water], should yield, after filtration, a further precipitate when more of the reagent is added."

Borax.—Two or three grammes is a convenient quantity.

$$\underbrace{Na_2B_4O_7 10,H_2O}_{\substack{2)382\\ \overline{\;191\;}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{\;63\;}}} = Na_2C_2O_4 + H_2B_4O_7 + 12H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

Tincture of litmus is the indicator, and the titration may be carried on without heat. The liberation of boric acid colours the litmus wine-red. This is not regarded, the titration being continued until the bright red due to the action of free oxalic acid makes its appearance. The British Pharmacopœia requires Borax to be pure (= 100 per cent.).

Lead Acetate, and *Solution of Subacetate.*—Operate upon about three grammes of acetate of lead, and from five to ten grammes of solution of subacetate.

$$\underbrace{Pb2C_2H_3O_2,3H_2O}_{\substack{2)379\\ \overline{189\cdot 5}}}+\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}=\text{grammes in 1,000 c.c. of standard solution.}}}=PbC_2O_4+2HC_2H_3O_2+5H_2O$$

$$\underbrace{Pb_2O2C_2H_3O_2}_{\substack{4)548\\ \overline{137}}}+2(\underbrace{H_2C_2O_4,2H_2O}_{\substack{4)252\\ \overline{63}=\text{grammes in 1,000 c.c. of standard solution.}}})=2PbC_2O_4+2HC_2H_3O_2+5H_2O$$

The flask in which the estimation is being conducted should previously contain one-third of water. In the case of both acetate and solution of subacetate of lead, a little acetic acid should be added to prevent precipitation of basic salt on dilution. The only indicator of complete reaction is cessation of production of the precipitate—oxalate of lead. Both the British and United States Pharmacopœias require acetate of lead to be pure (100 per cent.) and solution of subacetate to contain nearly 25 per cent.

Lime Water, and *Saccharated Solution of Lime.*—Measure about half a litre of lime water for the estimation, and of saccharated solution weigh about 25 grammes. The following equations, etc., are quantitative expressions of the reactions :—

$$\underbrace{Ca2HO}_{\substack{2)74\\ \overline{37}}}+\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}=\text{1,000 c.c. of standard solution.}}}=CaC_2O_4+4H_2O$$

Or,
$$\underbrace{CaOH_2O}_{\substack{2)56\\ \overline{28}}}+\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}}=CaC_2O_4+4H_2O$$

Litmus is used as an indicator. Ten fluid ounces of lime-water, B.P., contain $6\frac{2}{3}$ grains of hydrate of calcium (Ca2HO) or 5 grains of lime (CaO).

Sodium. Caustic Potash and Soda. Potassium and Sodium Carbonates and Bicarbonates.— Litmus is the indicator throughout, and heat is used in all cases, for the caustic alkalies always contain some carbonate.

$$\underbrace{Na_2}_{\substack{2)46\\ \overline{23}}}+\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}=\text{grammes in 1,000 c.c. of standard solution.}}}=H_2+Na_2C_2O_4+2H_2O$$

$$\underbrace{2KHO}_{\substack{2)112\\ \overline{56}}}+\underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}=\text{grammes in 1,000 c.c. of standard solution.}}}=K_2C_2O_4,+4H_2O$$

$$\underbrace{2NaHO}_{\substack{2)80\\ \overline{40}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = Na_2C_2O_4 + 4H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

$$\underbrace{K_2CO_3}_{\substack{2)138\\ \overline{69}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = K_2C_2O_4 + CO_2 + 3H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

Or, $$\underbrace{K_2CO_3 + 16\% H_2O}_{\substack{2)164{\cdot}28\\ \overline{82{\cdot}14}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = K_2C_2O_4 + CO_2 = xH_2O$$

63 = grammes in 1,000 c.c. of standard solution.

$$\underbrace{Na_2CO_3}_{\substack{2)106\\ \overline{53}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = Na_2C_2O_4 + CO_2 + 3H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

Or, $$\underbrace{Na_2CO_3,10H_2O}_{\substack{2)286\\ \overline{143}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = Na_2C_2O_4 + CO_2 + 13H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

$$\underbrace{2KHCO_3}_{\substack{2)200\\ \overline{100}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = K_2C_2O_4 + 2CO_2 + 4H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

$$\underbrace{2NaHCO_3}_{\substack{2)168\\ \overline{84}}} + \underbrace{H_2C_2O_4,2H_2O}_{\substack{2)126\\ \overline{63}}} = Na_2C_2O_4 + 2CO_2 + 4H_2O$$

63 = grammes in 1,000 c.c. of standard solution.

Convenient quantities to operate with are: of sodium, ·4 or ·5 of a gramme, placed on 10 or 20 c.c. of water in a basin, the latter being immediately covered with a glass plate to preserve the face and hands from any caustic spirtings and to prevent loss of soda; of caustic potash, 1 gramme; caustic soda, ·5 to 1 gramme; potassium carbonate, or bicarbonate, 1 to 2 grammes; sodium carbonate, or bicarbonate, 2 to 3 grammes; dried sodium carbonate, ·5 to 1 gramme: and of solutions a corresponding quantity. The British Pharmacopœial requirements are: sodium, 97·5 per cent.; caustic potash or soda, 90 to 100 per cent. of KHO or NaHO; potassium carbonate, 97 to 100 per cent. of K_2CO_3 + 16 per cent. H_2O; sodium carbonate, 96 to 100 per cent. of $Na_2CO_3,10H_2O$; potassium and sodium bicarbonates, 100 per cent. respectively, of $KHCO_3$ and $NaHCO_3$.

The strength of soda ash used to be reported in terms of "soda"—that is, oxide of sodium ($Na_2O = 62$); the old molecular weight of carbonate of sodium, 54 (it should have been 53), derived from that of "soda," 32 (it should have been 31), being employed in Great Britain in reporting the strength of soda-ash. The true amount of soda equivalent to 54 parts of carbonate is 31·41 parts. A modern analyst having found the true amount of soda in a sample of soda-ash is even now occasionally asked to report 31 as 31·41 parts, or 53 of carbonate as 54, and other quantities in proportion to these figures.

Tartrates and Citrates of Potassium and Sodium.—When tartrates or citrates of alkali-metals are burned in the open air, the whole of the metal remains in the form of carbonate. Each molecular weight of a neutral tartrate gives one molecular weight of carbonate, and every two molecular weights of an acid tartrate give one molecular weight of carbonate. Advantage is taken of these reactions to estimate indirectly the quantity of citrate or tartrate in presence of substances with which they are generally associated. One or two grammes of any of these salts is a convenient quantity to operate upon. The ignition may be conducted in a platinum or porcelain crucible. A low red heat only should be used, and the vessel removed when complete carbonization has been effected—that is to say, when nothing remains but the carbonate and free carbon. The mixture is in this case treated with hot water, and the carbon separated by filtration. If too little heat has been used, and carbonization is not complete, the filtrate will be more or less coloured. If this should be the case, the operation must be repeated with a fresh quantity of material. The carbonate is titrated in the usual way. The following equations, etc., explain the reactions:—

$$\underbrace{2(K_2C_4H_4O_6,H_2O)}_{4)488} + 5\,0_2 = \underbrace{2K_2CO_3}_{4)276} + 6CO_2 + 4H_2O$$

122 69 equiv. to 1,000 c.c. of stand. oxalic acid sol.

$$\underbrace{(2KHC_4H_4O_6}_{2)376} + 5\,0_2 = \underbrace{K_2CO_3}_{2)138} + 7CO_2 + 5H_2O$$

188 69 equiv. to 1,000 c.c. of standard oxalic acid.

$$\underbrace{2K_3C_6H_5O_7}_{6)612} + 9\,0_2 = \underbrace{3K_2CO_3}_{6)414} + 9CO_2 + 5H_2O$$

102 69 equiv. to 1,000 c.c. of stand. oxalic acid sol.

$$\underbrace{2(KNaC_4H_4O_6,\ 4H_2O)}_{\substack{4)564\\ \overline{141}}} + 5\ O_2 = \underbrace{2KNaCO_3}_{\substack{4)244\\ \overline{61}\text{ equiv. to 1,000 c.c. of stand. oxalic acid sol.}}} + 6CO_2 + 12H_2O$$

It will be readily understood that in the first (for example) of the reactions just expressed, 122 weights of tartrate of potassium are equivalent to 69 weights of carbonate of potassium ; and as in a previous reaction it has been shown that 69 weights of carbonate of potassium are equivalent to 63 weights of oxalic acid, it follows that 122 weights of tartrate of potassium are equivalent to 63 weights of oxalic acid. Let these weights be grammes, and then 122 grammes of tartrate of potassium are equivalent to 63 grammes of oxalic acid, or to 1,000 c.c. of the standard solution of oxalic acid. If the substance estimated be a crude sample of tartrate of potassium, and the number of c.c. of oxalic acid used has been 15 c.c., then as 1,000 c.c. of the acid solution are to 122 grammes of tartrate of potassium, so are 15 c.c. of the solution to 1·830 grammes of tartrate of potassium. Now if the weight of the sample taken was 2 grammes, then as two grammes of the sample contain 1·830 of real tartrate of potassium, 100 will contain $x = 91·5$ per cent. of real tartrate. This salt is required to be 99 per cent. pure by the British Pharmacopœia. Trade samples are practically pure as a rule. If sulphate of calcium be present in these tartrates or citrates, loss of carbonate of potassium will ensue, sulphate of potassium being formed. In estimating acid tartrate of potassium, which is the salt most likely to contain sulphate of calcium, direct titration, without ignition, may be followed. — Seven or eight per cent. of tartrate of calcium is commonly present in genuine cream of tartar.——*Rochelle Salt* and *Benzoate of Sodium* should each be pure within 1 per cent.

Notes.

Alkalimetry.—The foregoing processes are often spoken of as those of *alkalimetry* (the measurement of alkalies).

Neutral Solution of Litmus may be made by digesting the commercial fragments in about fifteen or twenty times their weight of water for a few hours, decanting, dividing into two equal portions, adding acid to one till it is faintly red, then pouring in the other and mixing. The solution may be kept in a stoppered bottle, and occasionally exposed to the air. It should never be filtered, but allowed gradually to deposit.

Standard Sulphuric Acid may be used in the place of oxalic acid, 1,000 c.c. of the liquid containing half of the molecular weight of the pure acid in grammes. It is prepared by diluting sulphuric acid with fifteen or twenty times its bulk of distilled water, ascertaining how much of the acid liquid is required to exactly neutralize $\frac{1}{20}$ of the molecular weight of pure carbonate of sodium, taken in grammes (5·3), and adding water until the observed volume of acid is increased to 100 c.c., the whole of the fluid being similarly diluted.

Weighing.—In the case of substances which are liable to alter by exposure to air, it is important that a selected quantity should be weighed, rather than selected weights be accurately balanced by material, the former operation occupying much the shorter time.

Salts other than the official may be quantitatively analysed by the volumetric solutions of the Pharmacopœia, slight modifications of manipulation even enabling the processes to be adapted to fresh classes of salts. Ample instructions for extending operations in this manner will be found in Sutton's "Handbook of Volumetric Analysis."

QUESTIONS AND EXERCISES.

Describe the apparatus used in volumetric determinations.—One hundred cubic centimètres of solution of oxalic acid contain 6·3 grammes of the crystallized salt; work sums showing what weights of bicarbonate of potassium and anhydrous carbonate of sodium that volume will saturate. *Ans.*, 10 grammes and 5·3 grammes.—Show what weight of hydrate of potassium is contained in solution of potash 48·02 grammes of which are saturated by 50 c.c. of the standard solution of oxalic acid. *Ans.*, 5·83 per cent.—Calculate the percentage of hydrate of calcium in lime-water 438 grammes of which are neutralized by 20 c.c. of the volumetric solution of oxalic acid. *Ans.*, 0·1689.—Eight grammes of a sample of Rochelle salt, after ignition, etc., require 54·3 c.c. of the official oxalic acid solution for complete saturation; work sums showing what is the centesimal proportion of real salt present. *Ans.*, 95·7.

ESTIMATION OF ACIDS.

In the previous experiments a known amount of an acid has been used in determining unknown amounts of alkalies. In those about to be described a known amount of an alkali is employed in estimating unknown amounts of acids. The alkaline salt selected may be either a hydrate or a carbonate, but the former is to be preferred; for the carbonic acid set free when a strong acid is added to a carbonate, interferes to some extent with the indications of alkalinity, acidity, or neutrality, afforded by litmus. The alkali most convenient for use is soda, a solution of which has probably already been made the subject of experiment in operations with the standard solution of oxalic acid. It should be kept in a stoppered bottle, and exposed to air as little as possible.

VOLUMETRIC SOLUTION OF SODA.

(Hydrate of Sodium, $NaHO = 40$.)

This aqueous solution of soda is most conveniently made of such a strength that each 1,000 c.c. contains one molecular weight in grammes of the alkali ($NaHO = 40$). It will be seen from the following equation that 40 grammes of soda convert 63 grammes of oxalic acid into neutral oxalate of sodium. Therefore one litre of this solution, containing 40 grammes of soda, will form a neutral solution of oxalate with one litre of standard oxalic acid solution, or with a chemically equivalent quantity of oxalic acid solution of any other strength :—

$$\underbrace{H_2C_2O_4,2H_2O}_{2)126} \quad + \quad \underbrace{2NaHO}_{2)80} \quad = \quad Na_2C_2O_4 + 4H_2O$$

$\overline{63}$ = 1,000 c.c. of stand. sol. $\overline{40}$ = 1,000 c.c. of standard solution.

If pure soda were at hand, it would only be necessary to weigh 40 grammes, dissolve this in water, and dilute to one litre. But pure soda cannot readily be produced. Therefore weigh about 45 grammes of hydrate of sodium of trade, and add water to one litre. When dissolved, take, say, 14 c.c., dilute with more water in a flask; add a few drops of tincture of litmus, and titrate with oxalic acid solution of known strength. Suppose that the volume of standard acid solution required to neutralize the 14 c.c. of soda solution the strength of which is to be estimated has been 15 c.c., or an equivalent amount of acid solution of another strength ; then, how many c.c. of soda solution are equivalent to 1,000 c.c. of standard acid solution ; or, what comes to the same thing, how many c.c. of soda solution contain forty grammes of real soda ($NaHO$)? As 15 c.c. stand. acid are to 14 c.c. soda sol., so are 1,000 c.c. stand. acid to x c.c. $x = 933$ c.c. 933 c.c. of the soda solution contain, therefore, 40 grammes of soda. This may either be diluted, every 933 c.c. to 1,000 c.c., so that it may be standard (1,000 c.c. = 40 grammes NaHO), or the solution may be used without dilution (933 c.c. = 40 grammes NaHO). It has already been mentioned that soda nearly always contains carbonate. To remove resulting carbonic acid, therefore, gentle heat should be employed towards the close of each titration in all the estimations with this solution. Litmus is used throughout as an indicator of completion of the reaction. The following substances are officially estimated with this solution. The list admits of considerable extension (*see* Sutton's "Volumetric Analysis").

Acetic Acid.—Operate upon about 1 gramme of glacial acid, about 20 grammes of diluted acid, or about 3 grammes of ordinary acetic acid.

$$\underbrace{HC_2H_3O_2}_{60} + \underbrace{NaHO}_{40\,=\,1{,}000\text{ c.c. standard solution.}} = NaC_2H_3O_2 + H_2O$$

Acetic Acid, B.P., should contain 33 per cent. of real acid ($HC_2H_3O_2$). Diluted Acetic Acid, B.P., 4·27 per cent. Glacial Acetic Acid, B.P., 99 per cent.

Citric Acid.—Operate on about 1 gramme. The reaction is expressed by the following equation, etc.:—

$$\underbrace{H_3C_6H_5O_7,H_2O}_{\substack{3)210\\ \overline{70}}} + \underbrace{3NaHO}_{\substack{3)120\\ \overline{40}\,=\,1{,}000\text{ c.c. standard solution.}}} = Na_3C_6H_5O_7 + 4H_2O$$

Citric Acid, B.P., should be pure (= 100 per cent. $H_3C_6H_5O_7,H_2O$).

Hydrochloric Acid.—Operate on from 1 to 2 grammes of the concentrated acid, or on about 4 grammes of the diluted acid.

$$\underbrace{HCl}_{36\cdot5} + \underbrace{NaHO}_{40\,=\,1{,}000\text{ c.c. standard solution.}} = NaCl + H_2O$$

Hydrochloric Acid, B.P., should contain 32 per cent. of real acid (HCl); and Diluted Hydrochloric Acid, B.P., 10·58 per cent. Diluted Hydrobromic Acid, 10 per cent. (HBr).

Lactic Acid, B.P., contains about 75 per cent. of real acid; Diluted Lactic Acid about 13 per cent.

Nitric Acid.—Operate on from 1 to 2 grammes of concentrated, or on 4 to 5 grammes of diluted acid.

$$\underbrace{HNO_3}_{63} + \underbrace{NaHO}_{40 = \text{grammes in 1,000 c.c. standard solution.}} = NaNO_3 + H_2O$$

Nitric Acid, B.P., should contain 70 per cent.; and Diluted Nitric Acid, B.P., 17·44 per cent. of real acid (HNO_3).

Nitrohydrochloric Acid.—Operate upon 4 to 5 grammes of diluted acid. The reaction is a complex one. The British Pharmacopœia requires that 35·2 grammes of the diluted acid should neutralize 88·3 c.c. of standard soda solution.

Sulphuric Acid.—Operate upon from ·5 to 1 gramme of concentrated acid, or from 4 to 5 grammes of either Diluted or Aromatic Sulphuric Acid.

$$\underbrace{H_2SO_4}_{\begin{array}{l}2)98\\ \quad\overline{49}\end{array}} + \underbrace{2NaHO}_{\begin{array}{l}2)80\\ \quad\overline{40} = \text{grammes in 1,000 c.c. standard solution.}\end{array}} = Na_2SO_4 + 2H_2O$$

Sulphuric Acid, B.P., should contain about 98 per cent.; Diluted, B.P., 13·65 per cent.; and Aromatic, B.P., about 12½ per cent. of real acid (H_2SO_4).

Tartaric Acid.—Operate upon about 1 gramme of the acid. The following equation, etc., represents the reaction:—

$$\underbrace{H_2C_4H_4O_6}_{\begin{array}{l}2)150\\ \quad\overline{75}\end{array}} + \underbrace{2NaHO}_{\begin{array}{l}2)80\\ \quad\overline{40} = \text{grammes in 1,000 c.c. standard solution.}\end{array}} = Na_2C_4H_4O_6 + H_2O$$

Tartaric Acid, B.P., should contain 99 per cent. of $H_2C_4H_4O_6$.

Notes.—1. Pure acetates, citrates more especially, tartrates, and some other organic salts, have an alkaline action on litmus, but not to an important extent. If the soda solution be added to acetic, citric, or tartaric acid, containing litmus, until the liquid is fairly blue, the operator will obtain trustworthy results; but in delicate experiments turmeric, "phenol-phthalein," etc., should be used instead of litmus. Phenol-phthalein, B.P., is "produced by reaction of phenol and phthalic anhydride. Its tincture yields an intense red colour with potash or soda, hence may be used as an indicator of the termination of volumetric reactions, especially those with organic acids." The "Tincture of Phenolphthalein," B.P., is made by dissolving 1 grain of phenolphthalein in 500 of proof spirit.

2. The operations for the quantitative analysis or measurement of acids are often collectively spoken of under the name of *acidimetry*.

QUESTIONS AND EXERCISES.

Calculate the percentage of real acid present in diluted sulphuric acid 30 grammes of which are neutralized by 84 c.c. of the official volumetric solution of soda. *Ans.*, 13·72.—Show how much real nitric acid is contained in a solution 36 grammes of which are saturated by 94 c.c. of the standard solution of soda. *Ans.*, 16·45 per cent.

ESTIMATION OF ACIDULOUS RADICALS PRECIPITATED BY NITRATE OF SILVER.

The purity of many salts and the strength of their solutions may be determined by this process; but only eight official substances (including diluted hydrocyanic acid, other cyanides, and some bromides and iodides) are quantitatively analysed by standard solution of nitrate of silver.

STANDARD SOLUTION OF NITRATE OF SILVER.

(Nitrate of Silver, $AgNO_3=170$.)

Dissolve 17 grammes of crystals of pure nitrate of silver in one litre of water. 1,000 c.c. of this solution contain $\frac{1}{10}$ of the molecular weight in grammes of nitrate of silver. It is therefore a decinormal solution.

If pure dry crystals of nitrate of silver are not at disposal, and pure dry crystals of chloride of sodium are at hand, a solution may be made of approximate strength and then be standardized by means of that salt. The method may be thus indicated:—

$$\underbrace{\mathrm{NaCl}}_{\substack{10)58{\cdot}5\\ \overline{\quad 5{\cdot}85}}} + \underbrace{\mathrm{AgNO_3}}_{\substack{10)170\\ \overline{\quad 17{\cdot}0}}} = \mathrm{AgCl} + \mathrm{NaNO_3}$$

17·0 = grammes in 1,000 c.c. standard solution.

Take rather less than ·1 gramme of the chloride of sodium ($NaCl$), and dissolve in water. The salt ($AgCl$) precipitated in the reaction is an insoluble salt, and the end of its precipitation will serve as a good indication of the completion of the reaction. A better indicator, however, is a few drops of neutral chromate of potassium (which previously was well purified by recrystallization). The nitrate of silver does not act upon the chromate until all the chloride is converted into chloride of silver, after which a deep red precipitate of chromate of silver is produced. This indication is extremely delicate, and in practice is noticed when the white colour due to chloride of silver changes to yellowish from formation of the first traces of chromate of silver. Solutions should be cool and not very dilute. The titration being accomplished, suppose that ·1 gramme of the chloride of sodium has taken 17 c.c. of the nitrate of silver solution of unknown strength; how many c.c. of the solution are equivalent to 5·85 of the chloride of sodium; that is, how many c.c. of solution contain 17 grammes of nitrate of silver? As ·1 gramme of $NaCl$ is to 17 c.c., so are 5·85 $NaCl$ to x c.c.$=$994 c.c. 994 c.c. of the solution of nitrate of silver are equivalent, therefore, to 1,000 c.c. of official standard solution, and contain 17 grammes of the nitrate of silver. They may be diluted to 1,000 c.c. if desired.

Hydrocyanic Acid.—Three to four grammes of *diluted* acid form a convenient quantity to operate upon. The HCN is first converted into KCN or $NaCN$, with potash or soda. The following equations, etc., explain the reactions:—

$$\underbrace{2HCN}_{\substack{10)54\\ \overline{\quad 5{\cdot}4}}} + 2NaHO = \underbrace{2NaCN}_{\substack{10)98\\ \overline{\quad 9{\cdot}8}}} + 2H_2O$$

$$\underbrace{2NaCN}_{\substack{10)98\\ \overline{\quad 9{\cdot}8}}} + \underbrace{AgNO_3}_{\substack{10)170\\ \overline{\quad 17{\cdot}0} = \text{grammes in 1,000 c.c. of standard solution.}}} = AgCN,NaCN + NaNO_3$$

It is seen that 5·4 grammes of real hydrocyanic acid (HCy) are equivalent to 9·8 grammes of cyanide of sodium, and represent 17 grammes of nitrate of silver, or 1,000 c.c. of standard solution of nitrate of silver.

The cyanide of sodium having been obtained, the titration is carried on until the salt is converted into the double salt

(NaCy,AgCy), immediately after which a permanent turbidity occurs, due to precipitation of cyanide of silver, thus:—

$$AgCy,NaCy + AgNO_3 = 2AgCy + NaNO_3.$$

The commencement of this turbidity forms a delicate and satisfactory proof of the completion of the above reaction.

There is, however, a difficulty in the conversion of the acid into the cyanide (Siebold), to which it is necessary to pay particular attention. Tincture of litmus is added to the acid diluted largely with water, and the soda poured in. Owing to the strong alkaline reaction of the cyanide of sodium formed, the mixture becomes blue when only a small proportion of the acid has been converted. If then the titration be conducted until the turbidity appears, only the cyanide of sodium will be estimated, leaving free hydrocyanic acid still unacted upon. Indeed cyanide of sodium may be estimated in presence of hydrocyanic acid in this way. Thus the following reaction (expressed approximately) might occur:—

$$\underbrace{NaCy + 4HCy}_{\text{Alkaline.}} + AgNO_3 = \underbrace{AgCy + NaNO_3 + 4HCy}_{\text{Turbid and acid.}}$$

In this case only one-fifth of the cyanogen originally present would be estimated. The mixture would, however, become acid. If this acidity be prevented, all difficulty is overcome. The following details (Senier) will be found to answer well. To the diluted hydrocyanic acid add soda solution until a strong alkaline reaction is shown by the tincture of litmus. Then add the silver solution drop by drop from the burette, when in most cases the mixture will become acid. When it does so, add more soda solution, and repeat this process until the final reading, when the solution must be alkaline. In this way the addition of too much soda at the commencement, which would use up silver solution and make the reading a trifle too high, is avoided.

Diluted Hydrocyanic Acid, B.P. and U.S.P., should contain 2 per cent. of real acid (HCN); *Aqua Laurocerasi*, B.P., 0·1 per cent.

Cyanide of Potassium.—0·1, in *dilute* solution, requires 7·3 c.c.; equivalent to 95 per cent. of real cyanide.

Bromide of Ammonium.—Take ·1 to ·2 gramme and conduct the titration in the same manner as for chloride of sodium, using chromate of potassium as an indicator:—

$$\underbrace{NH_4Br}_{\substack{10)\underline{98}\\ 9·8}} + \underbrace{AgNO_3}_{\substack{10)\underline{170}\\ 17·0}} = AgBr + NH_4NO_3$$

$17·0 =$ grammes in 1,000 c.c. of standard solution.

Bromide of Potassium.—Operate upon rather less than ·1 gramme, and conduct the titration in the same manner as with chloride of sodium, using chromate of potassium as an indicator of the close of the reaction.

$$\underbrace{KBr}_{\substack{10)\underline{119}\\ 11·9}} + \underbrace{AgNO_3}_{\substack{10)\underline{170}\\ 17·0}} = AgBr + KNO_3$$

$17·0 =$ grammes in 1,000 c.c. of standard solution.

The British Pharmacopœia requires bromide of potassium to contain 98 to 100 per cent. of the salt, and *bromide of sodium* about 99 per cent.

Remembering that 170 parts of nitrate of silver ($AgNO_3 = 170$) decompose 119 of bromide of potassium ($KBr = 119$), while on the one hand they decompose as little as 74·5 of chloride of potassium ($KCl = 74·5$), and on the other hand as much as 166 parts of iodide of potassium ($KI = 166$), it will be seen that the quantitative operation of the chloride as an impurity may neutralize the quantitative operation of the iodide. Hence the necessity to test the bromide qualitatively as well as quantitatively, and, as regards either impurity singly, of fixing maximum as well as minimum limits of the action of the volumetric solution of nitrate of silver on bromide of potassium. "Ten grains require for complete decomposition not less than 838 nor more than 850 grain-measures of the volumetric solution of nitrate of silver."

Iodide of Potassium.—0·2 should require 12·04 c.c. The salt is often 98 or 99 per cent. pure, containing not more than 0·5 per cent. of chloride, a little sulphate and a little carbonate. *Iodide of Sodium.*—0·1 should require 9·6 c.c., equivalent to 99 per cent. of real iodide.

Iodide of Potassium may be volumetrically estimated by a semi-decinormal solution of mercuric chloride, the termination of the operation being indicated by the commencement of the formation of a red precipitate:—

(1) $4KI + HgCl_2 = 2KCl + HgI_2,2KI$ (soluble).
(2) $HgI_2,2KI + HgCl_2 = 2KCl + 2HgI_2$ (insoluble).

The author of this process, M. Personne, stated (in 1875) that neither chlorides, bromides, nor carbonates interfere. Carles dissolves the iodide in spirit of wine of 17½ per cent., as much excess of water may decompose the double iodides.

Iodide of Iron.—Messrs. Naylor and Hooper (in 1881) demonstrated that Personne's solution is applicable to ferrous iodide, even in the state of syrup:—

(1) $2FeI_2 + HgCl_2 = FeCl_2 + FeI_2,HgI_2$ (soluble).
(2) $FeI_2,HgI_2 + HgCl_2 = FeCl_2 + 2HgI_2$ (insoluble).

The use of mercuric chloride for estimating the strength of syrup of iodide of iron was first suggested by E. Smith in 1859. The process was improved by T. & H. Smith in 1860.

Arseniate of Sodium.—The crystals of $Na_2HAsO_4,12H_2O$ lose water so readily that they cannot be relied upon to be represented by that formula. After the loss of five molecules of water another definite crystalline form ($Na_2HAsO_4,7H_2O$) remains. The amount of water of crystallization is estimated by drying at 300° F.

$$\underbrace{Na_2HAsO_4,12H_2O}_{402} = \underbrace{Na_2HAsO_4}_{186} + \underbrace{12H_2O}_{216}$$

It will be evident from the above equation that 402 grammes of the hydrous arseniate ($Na_2HAsO_4,12H_2O$) are equivalent to 186 grammes of the anhydrous (Na_2HAsO_4); in other words, that crystals of the former lose 53·73 per cent. of water by desiccation. In the British Pharmacopœia of 1867, arseniate of sodium was estimated by titration with standard solution of nitrate of silver, a sufficient quantity of soda to convert it into tri-sodium arseniate being first added. The completion of the reaction was indicated by a precipitate no longer forming with more of the silver solution. As the termination of the reaction is ill-defined, and the amount of soda to be added can only be ascertained when the amount of arseniate is already known, this method is very unsatisfactory, hence the salt is now estimated officially by precipitation with acetate of lead. A good method of estimating arseniate of sodium is to treat it with sulphurous acid, and, after boiling—to expel excess of the latter—to titrate the resulting arsenite with volumetric solution of iodine:—

$$\underbrace{Na_2HAsO_4}_{\substack{20)\underline{186}\\ \quad 9{\cdot}3}} + H_2SO_3 = \underbrace{Na_2HAsO_3}_{\substack{20)\underline{170}\\ \quad 8{\cdot}5}} + H_2SO_4$$

$$\underbrace{Na_2HAsO_3}_{\substack{20)\underline{170}\\ \quad 8{\cdot}5}} + \underbrace{I_2}_{\substack{20)\underline{254}\\ \quad 12{\cdot}7}} + H_2O = Na_2HAsO_4 + 2HI$$

12·7 = grammes in 1,000 c.c. of standard solution.

Spirit of Wine (*Spiritus Rectificatus*, B.P.) may contain traces of amylic alcohol and aldehyde; these may be detected by nitrate of silver, which is reduced by them to the metallic state. Any quantity beyond a mere trace of such bodies renders spirit of wine too impure for use in medicine. "Four fluid ounces with thirty grain-measures (about two c.c.) of the volumetric solution of nitrate of silver exposed for twenty-four hours to bright light, and then decanted from the black powder which has formed, undergoes no further change when again exposed to light with more of the test."

QUESTIONS AND EXERCISES.

Explain the volumetric method of estimating the strength of aqueous solutions of hydrocyanic acid.—Work a sum showing how much nitrate of silver will indicate, by the official volumetric process, the presence of 1 part of real hydrocyanic acid. *Ans.*, 3·148 parts.

ESTIMATION OF SUBSTANCES READILY OXIDIZED.

Any deoxidizer, that is, any substance which quickly absorbs a definite amount of oxygen, or is susceptible of any equivalent action, may be quantitatively tested by ascertaining how much of an oxidizing agent of known power must be added to a given quantity before complete oxidation is effected. The oxidizing agents employed for this purpose in the British Pharmacopœia are iodine and the red chromate of potassium. Permanganate of potassium is often used for the same purpose. Iodine acts indirectly, by taking hydrogen from water and liberating oxygen; the red chromate of potassium directly, by the facility with which it yields three-sevenths of its oxygen—as indicated by the equations and statements given on p. 764; permanganate of potassium, by affording five-eighths of its oxygen in presence of acid,

$$2K_2Mn_2O_8 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2.$$

STANDARD SOLUTION OF IODINE.

(Iodine, I = 127.)

If pure iodine be not at hand, it may be prepared by mixing the commercial article with about a fourth of its weight of iodide of potassium and subliming. Sublimation may be effected by gently warming the mixture in a beaker, the mouth of which is closed by a funnel; the iodine vapour condenses on the funnel, while fixed impurities are left behind, and any chlorine which the iodine may contain is absorbed by the iodide of potassium, an equivalent quantity of iodine being liberated. Small quantities may be similarly treated between two watch-glasses, placed edge to edge. Any trace of moisture in the resublimed iodine is removed by exposure for a few hours under a glass shade near a vessel containing oil of vitriol.

Place 12·7 grammes of pure iodine and about 18 grammes of pure iodide of potassium (an aqueous solution of which is the best solvent of iodine; the salt plays no other part in these operations) in a litre flask, add a *little* water and agitate until the iodine is dissolved; dilute to 1 litre.

The following substances are officially estimated by this volumetric solution :—

Sulphurous Acid.—Operate on about ·5 of a gramme of the acid, and dilute with water as usual. If the sulphurous acid be diluted to a less degree than ·04 or ·05 per cent., there will be some risk of the sulphuric acid formed being again reduced to sulphurous acid, with liberation of iodine. In delicate experiments the distilled water used for dilution should previously be freed from air by boiling, to prevent the small amount of oxidizing action which dissolved air would exert. The solution of iodine is then added until a slight permanent brown tint is produced, showing the presence of free iodine. A better indicator of the termination of the reaction is mucilage of starch, which gives a blue colour with the slightest trace of free iodine.

The following equations, etc., show the reaction that takes place :—

$$\underbrace{H_2SO_3}_{\substack{20)82\\ \overline{4\cdot1}}} + H_2O + \underbrace{I_2}_{\substack{20)254\\ \overline{12\cdot7} = \text{grms. in 1,000 c.c. of stand. sol.}}} = 2HI + H_2SO_4$$

$$\underbrace{H_2O,SO_2}_{\substack{20)64\\ \overline{3\cdot2}}} + H_2O + \underbrace{I_2}_{\substack{20)254\\ \overline{12\cdot7} = \text{grms. in 1,000 c.c. of stand. sol.}}} = 2HI + H_2SO_4,$$

The official (B.P.) sulphurous acid should contain 5 per cent. of sulphurous anhydride (SO_2).

Arsenic.—About ·1 of a gramme of *solid arsenic*, accurately weighed, should be dissolved in the usual quantity of water, heated to boiling, by aid of about ·5 of a gramme of bicarbonate of sodium. The arsenious acid is only partly, if at all, converted into arsenite or arseniate of sodium; but the iodine reaction occurs more readily in an alkaline solution. When the liquid is quite cold, mucilage of starch is added, and the iodine solution allowed to flow in until, after well stirring, a permanent blue colour is produced.—The official *arsenical solution* already containing some carbonate of potassium, requires somewhat less bicarbonate of sodium. 10 grammes is a convenient quantity to operate upon. To this should be added the usual quantity of water and about ·3 of a gramme of bicarbonate of sodium. After boiling and cooling, the titration is carried on as before.—About 10 grammes of the official *solution of arsenic in diluted hydrochloric acid* is also a convenient quantity to operate upon. This quantity requires about ·6 of a gramme of bicarbonate of sodium. The usual quantity of water is added, and the titration performed as before. The following equation exhibits the reaction:—

$$\underbrace{As_2O_3}_{\substack{40)198\\ 4\cdot95}} + 5H_2O + \underbrace{2I_2}_{\substack{40)508\\ 12\cdot7 = \text{grammes in 1,000 c.c. standard sol.}}} = 4HI + 2H_3AsO_4$$

Arsenic, B.P., should contain 100 per cent., and both Solutions, B.P., contain about 1 per cent. of arsenic.

In the foregoing operation, if ebullition be continued longer than is necessary for the solution of the arsenic, more monocarbonate of sodium may be formed than will be re-converted into bicarbonate by the liberated carbonic acid; loss of iodine will then ensue. E. J. Woolley has shown that borax may be usefully employed in the place of the bicarbonate of sodium.

Antimony also passes from lower to higher active quantivalence under the influence of nascent oxygen, iodine, or an equivalent acidulous radical. The following equation illustrates the reaction with tartar emetic and iodine. The student should make several determinations on, say, 20 c.c. of a solution of 2 grammes of pure crystals of tartar emetic in 200 c.c. of water. To the 20 c.c. add about an equal amount of strong solution of bicarbonate of sodium, a couple of c.c. of starch mucilage, and then the iodine solution, until, after stirring, the blue colour is fairly persistent. The whole operation should be quickly conducted or a precipitate of antimonious hydrate will be formed, and it is only when in solution that the antimony is properly attacked. This process is by Mohr. It has been tested by Fresenius and in the Research Laboratory of the Pharmaceutical Society, and is trustworthy.

$$\underbrace{(KSbOC_4H_4O_6)_2,H_2O}_{\substack{40)664\\ \overline{16\cdot6}}} + \underbrace{2I_2}_{\substack{40)508\\ \overline{12\cdot7} = \text{grammes in 1,000 c.c. of standard sol.}}} + 3H_2O = 4HI + 2KHC_4H_4O_6 + 2HSbO_3$$

Hyposulphite of Sodium.—About ·4 of a gramme is a convenient quantity to employ. It is dissolved in water, starch mucilage added, and the iodine solution slowly run in, the whole being frequently stirred, until a permanent blue colour is produced.

In the previous reactions iodine has acted as an indirect oxidizing agent by uniting with the hydrogen and thus liberating the oxygen of water. In the present case it unites with an analogue of hydrogen, namely sodium, a new salt (tetrathionate of sodium) being also produced, thus :—

$$\underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)496\\ 24\cdot8}} + \underbrace{I_2}_{\substack{20)254\\ 12\cdot7 = \text{grammes in 1,000 c.c. of standard sol.}}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

The British Pharmacopœia requires absolute purity in the case of hyposulphite of sodium—or *thiosulphate of sodium* as it is now generally termed.

QUESTIONS AND EXERCISES.

Give equations illustrative of the reactions on which the use of a standard volumetric solution of iodine is based.—From what point of view is iodine an oxidizing agent?—What reagent indicates the termination of the reaction between deoxidizing substances and moist iodine?—How much sulphurous acid gas will cause the absorption of 2·54 parts of iodine in the volumetric reaction? *Ans.*, 0·64.—What quantity of iodine will be required, under appropriate conditions, to oxidize 5 parts of arsenic? *Ans.*, 12·828.—Find by calculation the amount of hyposulphite of sodium which will react with 13 parts of iodine in volumetric analysis. *Ans.*, 25·386.

Volumetric Solution of Red Chromate of Potassium.

(Red Chromate of Potassium, $K_2Cr_2O_7 = 295$.)

One molecule of red chromate of potassium in presence of an acid, under favourable circumstances, yields four atoms of oxygen to the hydrogen of the acid, leaving three available either for direct oxidation or for combination with the hydrogen of more acid, an equivalent proportion of acidulous radical being liberated for any required purpose.

When used as a volumetric agent, the red chromate always yields the whole of its oxygen to the hydrogen of the accompanying acid, a corresponding quantity of acidulous radical being set free—four-sevenths of this radical immediately combining with the potassium and chromium of the red chromate, three-sevenths becoming available. Ferrous salts may thus be converted into ferric with sufficient rapidity and exactitude to admit of the estimation of an unknown quantity of iron by a known quantity of the red chromate. As one atom of any liberated bivalent acidulous radical will convert two molecules of ferrous salt into one of ferric, one molecule of red chromate causes six of ferrous to become three of ferric, as shown in the following equation:—

$$K_2CrO_4, CrO_3 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4, Cr_23SO_4 + 7H_2O + 3(Fe_23SO_4).$$

The volumetric solution is made by dissolving 14·75 grammes ($\frac{1}{20}$ of a molecular weight in grammes) of red chromate of potassium in water, and diluting to one litre. It is used in determining the strength of the ferrous preparations. It is known that the whole of the ferrous has been converted to ferric salt when a small drop of the liquid placed in contact with a drop of a fresh and very dilute solution of ferricyanide of potassium, on a white plate, ceases to strike a blue colour.

If the red chromate employed in making this standard solution is not known to be pure and dry, the strength of the solution may be checked by dissolving a small accurately weighed piece of pianoforte wire (0·4 or 0·5) in diluted sulphuric acid in a small flask, warming, and then running in the solution of red chromate until conversion is effected.

The reactions which take place may be thus expressed:—

$$\underbrace{6Fe}_{\substack{20)336\\ 16{\cdot}8}} + 6H_2SO_4 = \underbrace{6FeSO_4}_{\substack{20)912\\ 45{\cdot}6}} + 6H_2$$

$$\underbrace{6FeSO_4}_{\substack{20)912\\ 45{\cdot}6}} + \underbrace{K_2Cr_2O_7}_{\substack{20)295\\ 14{\cdot}75 = \text{grammes in 1,000 c.c. standard solution.}}} + 7H_2SO_4 = K_2SO_4,Cr_23SO_4 + 7H_2O + 3(Fe_23SO_4)$$

It is evident that 16·8 grammes of iron are equivalent in the reactions to 14·75 of red chromate or 1,000 c.c. of standard solution of the chromate. Now suppose that 0·5 of a gramme of pianoforte wire has been employed, and the quantity of solution of red chromate of unknown strength used has been 28 c.c. How many c.c. of this solution contains 14·75 of red chromate, that is, how many c.c. must be required to oxidize ferrous salt containing 16·8 of iron? As ·5 of iron is to 28 c.c. sol., so are 16·8 of iron to x c.c. sol. =941 c.c. Of the supposed solution, then, 941 c.c. would contain 14·75 grammes of red chromate, and would be equivalent to 1,000 c.c. of standard solution. It might be employed without being diluted, or, better, be diluted to official standard strength.

For standardizing the solution of red chromate, instead of iron wire, the light-green crystals of the double *ferrous sulphate and sulphate of ammonium* ($FeSO_4,(NH_4)_2SO_4,6H_2O =$ 392) may be employed, for it is a very stable salt.

Special care should be taken in all these estimations of substances readily oxidized to avoid atmospheric oxidation. Flasks may usually be loosely corked, or corked closely with a gas exit-tube passing just beneath a little mercury, and in all cases the estimation should be performed quickly. When standardizing with iron wire, any slight oxidation may be remedied by a fragment of zinc, the last portions of which must be removed or dissolved before the titration is commenced.

The ferrous salt in the following substances is estimated officially by this solution.

Sulphate of Iron.—Operate on 1 to 2 grammes. Dissolve the sulphate in water and add excess of sulphuric acid; the preceding equation indicates the reaction.

Sulphate of iron, B.P., ought to contain 99 per cent. of real sulphate or 54·15 per cent. of anhydrous sulphate. The granulated sulphate of iron is titrated in the same way, and should be pure, containing 54·67 per cent. of anhydrous sulphate of iron. The dried sulphate should contain 87·09 per cent. of the anhydrous sulphate ($FeSO_4$).

Arseniate of Iron.—Operate upon 1 to 2 grammes. Dissolve in excess of diluted sulphuric or hydrochloric acid. Sulphuric acid is preferable in most cases, because ferrous sulphate absorbs oxygen much less readily than ferrous chloride. The reaction that occurs is shown in the following equation, the ferrous arseniate being converted into ferric arseniate:—

$$\underbrace{2(Fe''_3 2AsO_4)}_{\substack{20)892\\ 44\cdot6}} + 7H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{20)295\\ 14\cdot75 = \text{grms. in 1,000 c.c. stand. sol.}}} =$$

$$K_2SO_4,Cr_2 3SO_4 + Fe'''_2 3SO_4 + 2(Fe'''_2 2AsO_4) + 7H_2O.$$

Arseniate of iron, B.P., is supposed to contain about 10 per cent. of ferrous arseniate. The compound is more nearly a ferric than a ferrous arseniate.

Phosphate of Iron.—Operate upon 1 to 2 grammes. Proceed as with arseniate. The following equation indicates the reaction, the ferrous phosphate being converted into ferric phosphate:—

$$\underbrace{2(Fe'_3 2PO_4)}_{\substack{20)716\\ 35\cdot8}} + 7H_2SO_4 + \underbrace{K_2Cr_2O_7}_{\substack{20)295\\ 14\cdot75 = \text{1,000 c.c. of standard sol.}}} =$$

$$K_2SO_4, Cr_2 3SO_4 + Fe'''_2 3SO_4 + 2(Fe'''_2 2PO_4) + 7H_2O$$

The official (B.P.) requirement is about one-third of its weight of anhydrous ferrous phosphate, or 47 per cent. of $Fe_3(PO_4)_2, 8H_2O$.

Saccharated Carbonate.—Proceed as with arseniate, using about the same quantity:—

$$\underbrace{6FeCO_3}_{\substack{20)696\\ \quad 34\cdot8}}+13H_2SO_4+\underbrace{K_2Cr_2O_7}_{\substack{20)295\\ \quad 14\cdot75 = 1{,}000 \text{ c.c. of standard solution.}}}=K_2SO_4Cr_23SO_4+3(Fe_23SO_4)+13H_2O+6CO_2$$

The official (B.P.) strength in anhydrous carbonate is "about one-third." Trade samples yield from 20 to 30, and sometimes 35 per cent., according to the care with which oxidation has been prevented. The theoretical percentage obtainable from the ingredients is 45·5, the quantity that would be present if the compounds were anhydrous and unoxidized—conditions never obtained in practice. Howie has suggested that as hydrochloric acid is known to so rapidly convert ordinary sugar into inverted sugar as to render it easily attacked by chromic acid, while phosphoric acid very slowly affects sugar, the latter acid instead of the former should be employed in dissolving the saccharated carbonate of iron for volumetric analysis. Another mode of eliminating the action of sugar is to char with sulphuric acid before analysing.

Magnetic Oxide of Iron.—Use about the same quantity as of, and proceed as with, arseniate or phosphate. The reaction may thus be shown:—

$$\underbrace{6Fe_3O_4}_{\substack{20)1392\\ \quad 69\cdot6}}+31H_2SO_4+\underbrace{K_2Cr_2O_7}_{\substack{20)295\\ \quad 14\cdot75 \;=\; \text{grammes in } 1{,}000 \text{ c.c. of standard solution.}}}=K_2SO_4,Cr_23SO_4+9(Fe_23SO_4)+31H_2O$$

Or,

$$6(Fe_2O_3,\underbrace{FeO)}_{\substack{20)432\\ \quad 21\cdot6}}+31H_2SO_4+\underbrace{K_2Cr_2O_7}_{\substack{20)295\\ \quad 14\cdot75 \;=\text{grammes in } 1{,}000 \text{ c.c. of stand. solution.}}}=K_2SO_4,Cr_23SO_4+9(Fe_23SO_4)+31H_2O$$

Absolutely pure magnetic oxide of iron contains 31 per cent. of ferrous oxide. Oxidation occurs, however, during manufacture, as in the case of the ferrous salts just described.

Note.—The use of this volumetric solution in quantitative analysis admits of great extension. The student should at least employ it in the case of a few iron ores.

QUESTIONS AND EXERCISES.

Write equations explanatory of the oxidizing power of red chromate of potassium.—One hundred cub. cent. of an aqueous solution of red chromate of potassium contain $\frac{1}{200}$ of the molecular weight of the salt in grammes; with what weight of metallic iron, dissolved in hydrochloric acid, will this volume react? *Ans.*, 1·68 gramme.—If 8·34 grammes of impure crystallized ferrous sulphate, dissolved in acidulated water, require 93 c.c. of the standard solution of chromate for complete conversion into ferric salt, what percentage of ferrous sulphate is present? *Ans.*, 93.—Work a sum showing how much red chromate of potassium is required for the conversion of 10 parts of ferrous sulphate into ferric salt. *Ans.*, 1·768.—Show what quantity of pure ferrous carbonate is indicated by 1·475 part of red chromate as applied in volumetric analysis. *Ans.*, 3·48.—Prove what amount of official saccharated carbonate of iron is equivalent to ·7375 part of red chromate in the volumetric reaction. *Ans.*, 4·7.

ESTIMATION OF SUBSTANCES READILY DEOXIDIZED.

Any substance which quickly yields a definite amount of oxygen may be quantitatively tested by ascertaining how much of a deoxidizing agent of known power must be added to a given quantity before complete deoxidation is effected. The chief compounds which may be used for this absorption of oxygen (deoxidizers or reducing agents, as they are commonly termed) are hyposulphite of sodium, sulphurous acid, ferrous sulphate,* oxalic acid, arsenious acid. The first-named is officially employed; it is only used in the estimation of free iodine, and, indirectly, of chlorine and chlorinated compounds. Iodine and chlorine are regarded as oxidizing agents, because their great affinity for hydrogen enables them to become powerful indirect oxidizers in presence of water.

STANDARD SOLUTION OF HYPOSULPHITE OF SODIUM.

(Crystallized Hyposulphite of Sodium, $Na_2S_2O_3,5H_2O = 284.$)

Dissolve about 27 grammes of hyposulphite of sodium in a litre or less of water. Fill a burette with this solution, and allow it to flow into a beaker containing, say, 15 c.c. of the volumetric solution of iodine. until the brown colour of the iodine is just discharged—or, starch being added, until the blue iodide of starch is decolorized. (The latter affords the more delicate indication.) When iodine and hyposulphite of sodium react, two atoms of iodine remove two of sodium from two molecules of the hyposulphite, tetrathionate of sodium being formed, thus :—

---

* "Five grains of permanganate of potassium dissolved in water require for complete decoloration a solution of forty-four grains of granulated sulphate of iron acidulated with two fluid drachms of diluted sulphuric acid."—B.P.

$$\underbrace{I_2}_{\substack{20)254\\ 12\cdot7\,=\,\text{grms. of iod. in 1,000 c.c.}}} + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)496\\ 24\cdot8\,=\,\text{grms. of hypo. in 1,000 c.c}}} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

Now suppose the number of c.c. required to fully attack the 15 c.c. of standard iodine were 14 c.c., how many c.c. of this hyposulphite solution would be equivalent to 1,000 c.c. of standard iodine solution? In other words, how many c.c. would contain 24·8 grammes of hyposulphite? As 15 c.c. iodine sol. are to 14 c.c. hyposulph. sol., so are 1,000 iodine sol. to x hyposulph. sol. = 933 c.c. Therefore 933 c.c. of this solution of hyposulphite would contain 24·8 grammes of the salt, and be equivalent to 1,000 c.c. of the official standard solution. The 933 c.c. would be diluted to 1,000 c.c. or be used without dilution. In either case its strength would, as usual, be recorded on the label. The following substances are estimated officially by means of this solution.

Solution of Chlorine.—About 10 grammes are operated upon. Excess of iodide of potassium is added—that is, to 10 grammes of solution of chlorine, about half a gramme of iodide. An amount of iodine is set free by the chlorine exactly in proportion to their atomic weights. The titration is then conducted as already described. The following equations show the reactions :—

$$\underbrace{Cl_2}_{\substack{20)71\\ 3\cdot55}} + 2KI = \underbrace{I_2}_{\substack{20)254\\ 12\cdot7}} + 2KCl$$

$$\underbrace{I_2}_{\substack{20)254\\ 12\cdot7}} + \underbrace{2(Na_2S_2O_3,5H_2O)}_{\substack{20)496\\ 24\cdot8\,=\,\text{grammes in 1,000 c.c. of standard solution.}}} = 2NaI + Na_2S_4O_6 + 10H_2O$$

It is evident, then, that 1,000 c.c. of standard solution of hyposulphite of sodium, or a corresponding quantity of a solution of different strength, is equivalent to 3·55 grammes of chlorine gas. Solution of chlorine of the British Pharmacopœia contains ·6 per cent. of chlorine gas.

Iodine.—Solid iodine is dissolved in solution of iodide of potassium, and titrated as already described. About ·2 of a gramme is a convenient quantity to employ. 1,000 c.c. of standard hyposulphite solution is equivalent, as seen in the equation, to 12·7 of iodine. The British Pharmacopœa requires "iodine" to contain 100 per cent. of real iodine. It is assumed in this operation that the iodine has been shown by qualitative analysis to be free from chlorine and bromine. These elements resemble iodine in reacting upon hyposulphite of sodium, hence would reckon as iodine in a volumetric assay.

Chlorinated Lime.—Operate on from ·1 to ·2 of a gramme. Dissolve in the usual quantity of water, and add excess of iodide of potassium and diluted hydrochloric acid. ·1 to ·2 of a gramme of chlorinated lime would require ·4 to ·8 of a gramme of iodide of potassium. The following equations show the reactions:—

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2;$$

or, $$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The chlorine thus set free liberates an equivalent amount of iodine, and this is titrated as before. (*See* the equations for solution of chlorine, p. 769.) This chlorine, liberated from chlorinated lime by acids, is its available chlorine for indirect oxidizing action. It should correspond (B.P.) to 33 per cent.

Solution of Chlorinated Lime.—About 2 grammes is a convenient quantity to operate upon. 1 gramme of iodide of potassium and excess of acid should be added, and the available chlorine determined as in the case of the solid. The official (B.P.) requirement is about 2 to 3 per cent. of available chlorine.

Solution of Chlorinated Soda.—About 2 grammes are mixed with the usual quantity of water and about 1 gramme of iodide of potassium and excess of acid added. The available chlorine is estimated as in the case of chlorinated lime. The reaction by which the chlorine is evolved is familiar:—

$$NaCl, NaOCl + 2HCl = 2NaCl + H_2O + Cl_2.$$

The action of the liberated chlorine on the iodide of potassium and the iodine on the hyposulphite solution has been described under "solution of chlorine." The official (B.P.) requirement is about 2·5 per cent. of available chlorine.

QUESTIONS AND EXERCISES.

For what purpose is the official volumetric solution of hyposulphite of sodium used?—On what reaction is based the quantitative employment of hyposulphite of sodium?—How much hyposulphite of sodium is required to show the presence of 10 parts of iodine?—*Ans.*, 19·527.—Calculate the amount of chlorine 4·96 parts of hyposulphite of sodium are equivalent to in volumetric analysis. *Ans.*, ·71.—Describe the operations included in the estimation of the strength of bleaching-powders.—By what reagent is the complete absorption of free iodine by hyposulphite of sodium indicated?

QUESTIONS, WITH ANSWERS FOR VERIFICATION.

Work sums showing how much bicarbonate of potassium is contained in an eight-ounce bottle of medicine, seven fluid drachms of which are saturated by two and a half grains of crystallized oxalic acid. *Ans.*, 36·3 grains.—A sample of soda-ash is said to contain 78 per cent. of pure anhydrous carbonate of sodium: if the statement be true, how much of the official volumetric solution of oxalic acid will saturate 5 grammes of the specimen? *Ans.*, 73·6.—2·69 grammes of common brown sulphuric acid are saturated by 43·5 cubic centimètres of the official volumetric solution of soda; how much acid of 96·8 per cent. is present? *Ans.*, The 2·69 contain 2·2.—Four grammes of a litre and a half of concentrated hydrocyanic acid are equivalent to 89 cubic centimètres of volumetric solution of nitrate of silver of official strength; to what volume must the bulk of the acid be diluted for the production of acid of pharmacopœial strength? *Ans.*, 9 litres.—3·18 grammes of a powder containing arsenic require for complete reaction 84 cubic centimètres of a volumetric solution of iodine, which is 1·43 per cent. weaker than the standard solution of the British Pharmacopœia; what percentage of pure arsenic is contained in the powder? *Ans.*, 12·86.—How much pure metal is present in a sample of iron 1·68 gramme of which, dissolved in diluted sulphuric acid, is exactly attacked by 95·7 cubic centimètres of an official volumetric solution of red chromate of potassium which is ·6 per cent. too strong?

GRAVIMETRIC QUANTITATIVE ANALYSIS.

(*For preliminary remarks on the general principles of gravimetric analysis and the relation of gravimetric and volumetric analyses to each other, see pages* 706 *and* 707.)

ESTIMATION OF METALS.

POTASSIUM.

Outline of the process.—This element is usually estimated in the form of double chloride of potassium and platinum. Qualitative analysis having proved the presence of potassium and other radicals in a substance, a small quantity of the material is accurately weighed, dissolved, and the other elements removed by appropriate reagents: the precipitates are well washed, in order that no trace of the potassium salt shall be lost, the resulting liquid concentrated over a water-bath (to avoid loss that would occur mechanically during ebullition), hydrochloric acid added if necessary, solution of perchloride of platinum poured in, and evaporation continued to dryness: excess of the perchloride is then dissolved out by adding, to the dried residue, spirit of wine containing half its bulk of ether (a liquid in which the double chloride is insoluble), the mixture is carefully poured on to a tared and dried filter, washed with the spirit till every trace of free perchloride of platinum is removed, and the whole dried and weighed; from the resulting amount the proportion of potassium, or equivalent quantity of a salt of potassium, is ascertained by calculation.

> *Note.*—From this short description it will be seen, first, that the chemistry of quantitative analysis is the same as that of qualitative; and secondly, that the principle of gravimetic is the same as that of volumetric quantitative analysis:—the combining-proportions of substances being known, unknown quantities of elements may be ascertained by calculation from known quantities of their compounds.

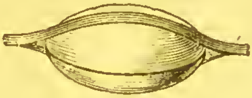
Apparatus.—In addition to a delicate balance and weights and the common utensils, a few special instruments are used in quantitative manipulation; some of these may be prepared before proceeding with the estimation of potassium.

Filtering-paper may be of the kind known as "Swedish," the texture of which is of the requisite degree of closeness, and its ash small in amount. A large number of circular pieces of one size, six to eight centimètres in diameter, should be cut ready for use. In delicate experiments, where a precipitate on a filter has to be ignited and the paper subsequently burnt, the weight of the ash of the filter must be deducted from the weight of the residue. The ash is estimated after burning ten or twenty of the cut filters. These are folded into a small compass, a portion of a piece of platinum wire twisted a few times round the packet, so as to form a cage, the whole held by the free end of the wire over a weighed porcelain crucible placed in the centre of a sheet of glazed paper, the bundle ignited by a spirit-lamp or smokeless gas-flame, the flame allowed to impinge against the charred mass till it falls into the crucible below, any stray fragments on the sheet carefully shaken into the crucible, the latter placed over a flame till carbon has all burnt off, and nothing but ash remains, the whole cooled, weighed, and the weight of the crucible deducted; the weight of the residue divided by the number of pieces used gives the average amount of ash in each filter.

Fig. 75.

A PAIR OF WEIGHING-TUBES.

Fig. 76.

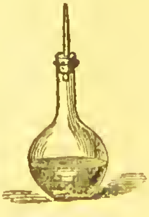


CLAMPED WATCH-GLASSES FOR WEIGHING.

A pair of weighing-tubes (fig. 75), for holding dried filters during operations at the balance, may be made from two test-tubes, one fitting closely within the other. About five centimètres of the closed end of the outer and seven of the inner are cut off by leading a crack round the tube with a pencil of incandescent charcoal, and the sharp edges fused in the blowpipe-flame. A filter, after drying, is quickly folded and placed in the narrower tube, the mouth of which is then closed by the wider tube. This prevents reabsorption of moisture from the air. *A pair of watch-glasses*, having accurately ground edges and clamped as shown in figure 76, also forms a convenient arrangement for weighing filters, etc.

The washing-bottle (fig. 77), holding the *spirit of wine and ether*, is a common flask, through the cork of which a short straight tube passes. The outer end of the tube should be sufficiently narrowed to enable it to deliver a very fine stream of the liquid. The flask being inverted, the warmth of the hand expands the air and vapour to a sufficient extent to force out the liquid.

Fig. 77.



The ordinary washing-bottle for quantitative operations should be formed of a flask in which water may be boiled, fitted up as usual (*vide* p. 119).

A Water-oven is the best form of drying-apparatus. It is a small square copper vessel, jacketed on five sides and having a door on the sixth; water is poured into the space between the inner and outer casing, and the whole placed over a gas-lamp or other source of heat, moist air and steam escaping by appropriate apertures. Desiccation at higher temperatures than the boiling-point of water may be practised by using oil or paraffin instead of water, inserting a thermometer in the fat. The apparatus may be purchased of any maker of chemical instruments.

Pure distilled water must be used in all quantitative determinations.

> *Note.*—In practising the operations of quantitative analysis, experiments should at first be conducted on definite salts of known composition, for the accuracy of results may then be tested by calculation.

Estimation of potassium in the form of double chloride of potassium and platinum.—Select two or three crystals of pure nitrate of potassium, powder them in a clean mortar, dry the powder by gently heating in a porcelain crucible over a flame for a few seconds, place about a couple of décigrammes (0·2 grm.) of the powder in a counterpoised watch-glass, accurately weigh the selected quantity, transfer to a small dish, letting water from a wash-bottle flow over the watch-glass and run into the dish, warm the dish till the nitrate is dissolved, acidulate with hydrochloric acid, add excess of aqueous solution of perchloride of platinum (a quantity containing about 0·4 of solid salt), evaporate to dryness over a water-bath. While evaporation is going on, place a filter and the weighing-tubes in the water-oven, exposing them to a temperature of 100° C. for about half an hour; fold the filter and insert it in the tubes, place them on a plate under a glass shade, and when cold accurately note their weight. Arrange the weighed filter in a funnel over a beaker.

Transfer the dried and cooled platinum salt from the dish to the filter by moistening the residue with the mixture of alcohol and ether and, when the salt is loosened, pouring the contents of the dish into the paper cone. Any salt still adhering may be freed by the finger, which, together with the dish, should be washed in the stream of spirit, the rinsings at once flowing into the filter. The filtrate should have a yellowish-brown colour, due to the excess of perchloride of platinum. If it is colourless, an insufficient amount of perchloride has been added, and the whole operation must be repeated. The washed precipitate and filter are finally dried in the water oven, folded and placed in the weighing-tubes, the drying and weighing when cold being repeated until the whole ceases to alter; the final weight being noted.

Desiccators.—Highly dried substances are very hygroscopic, hence before being weighed should be cooled under a bell-jar which also encloses a vessel containing sulphuric acid or chloride of calcium—*a desiccator*. (If filters are not freed from all traces of acid by thorough washing, the paper will be brittle when dry, falling to pieces on being folded.)

Analytical memoranda may have the following form:—

Watch-glass and substance . . . .
Watch-glass . . . . ________
Substance . ________

Weighing-tubes, filter, and Pt. salt . . . . .
Weighing tubes and filter . . . . ________
$PtCl_4$, 2KCl. ________

The calculations are simple:—

$$\text{As}\left\{\begin{matrix}PtCl_4, 2KCl\\=484{\cdot}8\end{matrix}\right\}\text{is equivalent to}\left\{\begin{matrix}2KNO_3\\=202\end{matrix}\right\},$$

$$\text{so}\left\{\begin{matrix}\text{the weight of}\\\text{double chloride}\\\text{obtained}\end{matrix}\right\}\text{is equivalent to } x.$$

x will be the amount of pure nitrate of potassium in the quantity of substance operated on. x should in the present instance be identical with the weight of substance taken, because, for educational purposes, pure nitre is under examination. Only after analyses of pure substances have yielded the operator results practically identical with those by calculation, can analyses of substances of unknown degree of purity be undertaken with confidence. A table of atomic weights, from which to find molecular weights, is given in the Appendix. Cl=35·5, or, more exactly, 35·4.

Platinum Residues should be preserved, and the metal recovered from them from time to time (*vide* p. 288).

Hot alcohol sometimes reduces perchloride of platinum, the metal being thrown out of solution in a finely divided form, known as *platinum black ;* only aqueous solutions, therefore, of the salt should be used where heat is employed. Hence, also, in washing out excess of perchloride of platinum from the double chloride of platinum and potassium by spirit, the application of heat should be avoided.

Effervescing Potash-water (*Liquor Potassæ Effervescens*, B.P.) is most easily estimated volumetrically (p. 748). Any adulteration by an equivalent amount of bicarbonate of sodium would, however, by that process be undetected; hence the Pharmacopœia directs that "five fluid ounces, evaporated to one-fifth and 12 grains of tartaric acid added, yield a crystalline precipitate, which when dried weighs not less than 12 grains." Five fluid ounces of this preparation should contain 7·5 grains of bicarbonate, convertible into 14·1 grains of acid tartrate of potassium by 11·25 grains of tartaric acid. The method is somewhat rough, but quite efficient for "potash-water" containing nothing but bicarbonate of alkali-metals.

Proportional Weights of Equivalent Quantities of Potassium and its Salts.

Metal	K_2	78
Oxide ("Potash")	K_2O	94
Hydrate ("Caustic Potash")	2KHO	112
Carbonate (anhydrous)	K_2CO_3	138
Carbonate (crystalline)	$K_2CO_3 + 16\%$ Aq.	164·285
Bicarbonate	$2KHCO_3$	200
Nitrate	$2KNO_3$	202
Platinum salt	$PtCl_4, 2KCl$	484·8

SODIUM.

Sodium is usually estimated as sulphate. Accurately weigh a porcelain crucible and lid, place within about ·3 of pure rock-salt, and again weigh, making a memorandum of the weights in a note-book. Add rather more strong sulphuric acid than may be considered sufficient to convert the chloride into acid sulphate of sodium. Heat the crucible gradually, the flame being first directed against the side of the crucible to avoid violent ebullition, until fumes of acid cease to be evolved, towards the end of the operation dropping in one or two fragments of carbonate of ammonium to facilitate complete expulsion of all excess of acid. When cold, weigh the crucible and contents. The weight of the crucible having been deducted, the amount of sulphate obtained should be the exact equivalent of the quantity of chloride of sodium employed.

$$\underbrace{2NaCl}_{116{\cdot}8} + H_2SO_4 = \underbrace{Na_2SO_4}_{142} + 2HCl.$$

Proportional Weights of Equivalent Quantities of Sodium and its Salts.

Metal	Na_2	46
Oxide ("Soda")	Na_2O	62
Hydrate ("Caustic Soda")	$2NaHO$	80
Carbonate (anhydrous)	Na_2CO_3	106
Carbonate (crystals)	$Na_2CO_3,10H_2O$	286
Bicarbonate	$2NaHCO_3$	168
Chloride	$2NaCl$	116·8
Sulphate (anhydrous)	Na_2SO_4	142
Sulphate (crystals)	$Na_2SO_4,10H_2O$	322

AMMONIUM.

Salts of ammonium are, for purposes of quantitative analysis, generally converted into the double chloride of ammonium and platinum ($PtCl_4 2NH_4Cl$), the details of manipulation being the same as those observed in the case of potassium (p. 774). About 0·15 grm. of pure, white, dry, chloride of ammonium may be taken for experiment.

Composition of the Platinum Salt.

		In 1 molec. wt.	In 100 parts.
Pt	194·4	194·4	43·903
Cl_6	35·4 × 6	212·4	47·967
N_2	14·0 × 2	28	6·324
H_8	1·0 × 8	8	1·806
		442·8	100·000

		In 1 molec. wt.	In 100 parts.
or, $PtCl_4$	336	336	75·88
$2NH_4Cl$	53·4 × 2	106·8	24·12
		442·8	100·00

The proportion of nitrogen, ammonium, or chloride of ammonium in the double chloride may also be ascertained from the weight of platinum left on igniting the double chloride; indeed, this operation *must* be performed if any variety of ammonium other than the ordinary hydrogen ammonium may be present. The heat must be applied slowly, or platinum will be mechanically carried off with the gaseous products of decomposition.

Proportional Weights of Equivalent Quantities of Ammoniacal Compounds.

Ammonia (gas)	$2NH_3$	34
Ammonium	$(NH_4)_2$?	36
Chloride of ammonium	$2NH_4Cl$	106·8
Platinum salt	$PtCl_4,2NH_4Cl$	442·8
" Carbonate of ammonium "	$(N_3H_{11}C_2O_5) \div 3 \times 2$	104·7
Sulphate of ammonium	$(NH_4)_2SO_4$	132

BARIUM.

Barium is estimated in the form of anhydrous sulphate of barium ($BaSO_4$). Ba = 136·8.

Process.—Dissolve 0·3 or 0·4 of pure crystallized and dried chloride or nitrate of barium in about half a litre of water in a beaker, heating to incipient ebullition, and slightly acidulating with hydrochloric or nitric acid. Add diluted sulphuric acid (prepared some days previously, so that sulphate of lead may have deposited) so long as a precipitate forms, keep the mixture hot for some time, set aside for half an hour, pass the supernatant liquid through a filter, gently boil the residue twice or thrice with acidulated water; finally collect the precipitate on the filter, removing ahherent particles from the beaker by the finger, and cleansing by a stream of hot water from the wash-bottle. The precipitate must be washed with hot water until the filtrate ceases to turn litmus-paper red, or give any cloudiness when tested with chloride of barium. The filter and sulphate of barium, having thoroughly drained, is dried in a warm place, commonly by supporting the funnel in an inverted bottomless beaker over a sand-bath or hot plate.

The sulphate of barium is now removed from the filter, heated to drive off every trace of moisture, and weighed. This is accomplished by placing a weighed porcelain crucible (and cover) on a sheet of glazed paper, holding the filter over it, and carefully transferring the precipitate; the sides of the filter are then gently rubbed together and detached powder dropped into the crucible, the paper folded, encased in two or three coils of one end of a platinum wire, and burnt over the crucible, ash and any particles on the sheet of paper dropped into the sulphate of barium, the open crucible exposed over a flame till its contents are quite white, covered, cooled, and weighed.

	Formulæ.	Molecular Weights.
Chloride of barium	$BaCl_2,2H_2O$ . . .	243·6
Nitrate of barium	$Ba2NO_3$	260·8
Sulphate of barium	$BaSO_4$	232·8

Composition of Sulphate of Barium.

		In 1 molec. wt.	In 100 parts.
Ba	136·8 . . .	136·8 . . .	58·77
S	32 . . .	32 . . .	13·73
O_4	16×4 . . .	64 . . .	27·50
		232·8	100·00

In the first four or five educational experiments it is not essential to take filter-ash into account. Mistakes of manipulation due to inexperience may cause far greater errors.

CALCIUM.

Calcium is usually thrown out of solution in the form of oxalate, the precipitate ignited, and the resulting carbonate weighed.

Process.—Dissolve 0·3 or 0·4 of dried colourless crystals of calc-spar in about a third of a litre of water acidulated with hydrochloric acid, heat the solution to near the boiling-point, add excess of solution of oxalate of ammonium, then ammonia until, after stirring, the liquid smells strongly ammoniacal; set aside in a warm place for twelve hours. Carefully pour off the supernatant liquid, passing it through a filter; add hot water to the precipitate, set aside for half an hour, again decant, and, after once more washing, transfer the precipitate to the filter, allowing all contained fluid to pass through before a fresh portion is added. Wash the precipitate with hot water, avoiding a rapid stream, or the precipitate may be driven through the pores of the paper. Dry, transfer to a weighed crucible, and incinerate, as described for sulphate of barium, and slowly heat the precipitate till the bottom of the crucible is just visibly red when seen in the dark. As soon as the residue is white or only faintly grey, remove the lamp, cool, and weigh.

The resulting carbonate of calcium should have the same weight as the calc-spar from which it was obtained. If loss has occurred, carbonic acid gas has probably escaped. In that case moisten the residue with water, and after a few minutes test the liquid with red litmus or turmeric paper; if an alkaline reaction is noticed, it is due to the presence of caustic lime. Add a small lump of carbonate of ammonium, evaporate to dryness over a water-bath, and again ignite, this time being careful not to go beyond the prescribed temperature. The treatment may, if necessary, be repeated.

Proportional Weights of Equivalent Quantities of Calcium and its Salts.

Metal	Ca	40
Oxide (quicklime)	CaO	56
Hydrate (slaked lime)	$Ca2HO$	74
Carbonate	$CaCO_3$	100
Sulphate (anhydrous)	$CaSO_4$	136
Sulphate (crystalline or precipitated)	$CaSO_4,2H_2O$	172
Chloride	$CaCl_2$	110·8
Phosphate (of bones)	$(Ca_32PO_4)\div 3$	103·3

MAGNESIUM.

Process 1.—*The light or heavy carbonate of magnesium* of pharmacy may be estimated by heating a weighed quantity to redness in a porcelain crucible. If it has the composition indicated by the formula given in the British Pharmacopœia ($3MgCO_3$, $Mg2HO$, $4H_2O$), it will yield 42 per cent. of magnesia (MgO). According to that work, the purity of even sulphate of magnesium ($MgSO_4,7H_2O$) may be determined by boiling a weighed quantity with excess of carbonate of sodium, collecting the precipitate, washing, drying, igniting, and weighing the resulting magnesia (MgO). The crystallized sulphate should afford 16·26 per cent. of oxide. The official solution of carbonate of magnesium in carbonic acid water (*Liquor Magnesii Carbonatis*, B.P.) should yield about four grains of pure oxide of magnesium per fluid ounce.

Process 2.—*The general form in which magnesium is precipitated* is as phosphate of ammonium and magnesium ($MgNH_4PO_4,6H_2O$); this, by heat, is converted into pyrophosphate of magnesium ($Mg_2P_2O_7$). Accurately weigh a small quantity (0·4 to 0·5) of pure dry crystals of sulphate of magnesium, dissolve in two to three hundred cubic centimètres of cold water in a beaker, add chloride of ammonium, ammonia, and phosphate of sodium or ammonium, agitate with a glass rod (without touching the sides of the vessel, or crystals will firmly adhere to the rubbed portions), and set aside for twelve hours. Collect on a filter, wash the precipitate with water containing a tenth of its volume of the strongest solution of ammonia, until the filtrate ceases to give a precipitate with an acidulated solution of nitrate of silver. Dry, transfer to a crucible, burn the filter in the usual way, heat slowly to redness, cool, and weigh.

Proportional Weights of Equivalent Quantities of Magnesium Salts.

Pyrophosphate	$Mg_2P_2O_7$	222
Sulphate	$2(MgSO_4, 7H_2O)$	492
Oxide	$2(MgO)$	80
Official carbonate	$(3MgCO_3, Mg2HO, 4H_2O) \div 2$	191

ZINC.

Zinc is usually estimated as oxide (ZnO), occasionally as sulphide (ZnS). $Zn = 64{\cdot}9$.

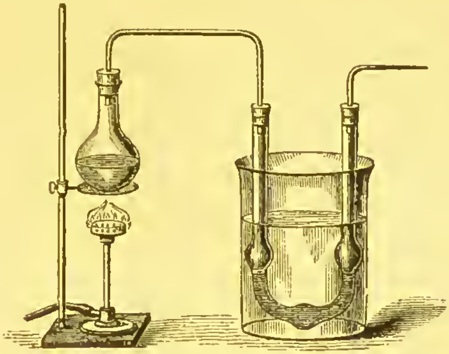
Process.—Dissolve a weighed quantity (0·5 to 0·6) of sulphate of zinc in about half a litre of water in a beaker, heat to near the boiling-point, add carbonate of sodium in slight excess, boil, set aside for a short time; pass the supernatant liquid through a filter, gently boil the precipitate with more water, again decant; repeat these operations two or three times; collect the precipitate on the filter, wash, dry, transfer to a crucible, incinerate, ignite, cool, and weigh. 286·9 (=molec. weight) of sulphate should yield 80·9 (=molec. weight) of oxide.

MANGANESE.

To ascertain its value for evolving chlorine from hydrochloric acid, a weighed quantity of finely powdered black oxide of manganese is heated in a small flask with pure hydrochloric acid (contained in an inner tube as for "oxalates" and "carbonates," p. 801), and the resulting chlorine conveyed into a U-tube containing solution of iodide of potassium. (*See* fig. 78.) The amount of iodine thus freed is estimated by the volumetric solution of hyposulphite of sodium. 126·6 of iodine indicate 35·4 of chlorine.

Manganese may also be estimated by the reaction and apparatus described under "Oxalates," p. 802.

Fig. 78.



ALUMINIUM.

Aluminium is always precipitated as hydrate (Al_26HO) and weighed as oxide (Al_2O_3).

Process.—Dissolve about two grammes of pure dry ammonium-alum in half a litre of water, heat the solution, add chloride of ammonium and a slight excess of ammonia, boil gently till the odour of ammonia has nearly disappeared, set aside for the hydrate to deposit, pass the supernatant liquid through a filter, wash the precipitate three or four times by decantation, transfer to the filter, finish the washing, dry, burn the filter, ignite in a covered crucible, cool, and weigh.

Al_23SO_4, K_2SO_4, $24H_2O$	948
Al_23SO_4, $(NH_4)_2SO_4$, $24H_2O$	906
Al_2O_3	102
Per cent. of Al_2O_3 yielded by ammonium-alum .	11·26

QUESTIONS AND EXERCISES.

Give details of the manipulations observed in gravimetrically estimating salts of potassium or of ammonium.—What quantity of chloride of sodium is contained in a sample of rock-salt 0·351 of a gramme of which yields 0·426 of sulphate of sodium? *Ans.*, 99·83 per cent.—To what amount of the ammonium-alum is 0·888 of a gramme of the double chloride of platinum and ammonium equivalent? *Ans.*, 1·817 gramme. —Find the weight of sulphate of barium obtainable from 0·522 of nitrate? *Ans.*, 0·466.—Describe the usual method by which salts of calcium are estimated.—By what quantitative process may the official salts of magnesium be analysed?—Calculate the proportion of pure sulphate of zinc in a sample of crystals 0·574 of which yield 0·161 of oxide. *Ans.*, 99·4 per cent.—Ascertain the weight of alumina (Al_2O_3) which should be obtained from 1·812 of a gramme of ammonium-alum.

IRON.

Iron and its salts are gravimetrically estimated in the form of ferric oxide (Fe_2O_3).

Compounds containing organic acidulous radicals are simply incinerated, and the resulting oxide weighed. Thus 1 gramme of the official citrate of iron and ammonium (*Ferri et Ammonii Citras*, B.P.) incinerated, with exposure to air, leaves not less than ·27 of ferric oxide. A small quantity of the salt is weighed in a tared covered porcelain crucible, flame cautiously applied until vapours cease to be evolved, the lid then removed, the crucible slightly inclined and exposed to a red heat until all carbonaceous matter has disappeared. The residual ferric oxide is then weighed. The tartrate of potassium and iron (*Ferrum Tartaratum*, B.P.) is treated in the same manner, except that the ash must be washed and again heated before weighing, in order to remove carbonate of potassium produced during incineration; 5 grammes should yield about 1·5 gramme of ferric oxide.

From other compounds of iron, soluble in water or acid, the metal is precipitated in the form of hydrate (Fe_26HO) by solution of ammonia, and converted into oxide (Fe_2O_3) by ignition. Dissolve a piece (about 0·2) of the purest iron obtainable (piano-wire), accurately weighed, in water acidulated with hydrochloric acid; add a few drops of nitric acid, and gently boil; pour in excess of ammonia, stir, set aside till the ferric hydrate has deposited, pass the supernatant liquid through a filter, treat the precipitate three or four times with boiling water; transfer to the filter, wash till the filtrate yields no trace of chlorine (for chloride of ammonium will decompose ignited ferric oxide, with volatilization of ferric chloride), dry, and ignite as usual, and weigh. Iron in the official solutions (*Liquor Ferri Acetatis Fortior*, *Liquor Ferri Dialysatus*, *Liquor Ferri Perchloridi Fortior*, *Liquor Ferri Pernitratis*, and *Liquor Ferri Persulphatis*) is estimated by this general process.

The Proportion of metallic iron in a mixture of iron and oxides of iron may be determined by digestion in a strong solution of iodine and iodide of potassium, which attacks the metal only. The reduced iron of pharmacy (*Ferrum Redactum*, B.P.) is in good condition so long as it contains, as shown by this method, half its weight of free metal.

Another Method.—Reduced iron is converted into ferrous chloride by a hot, strong solution of corrosive sublimate, while the oxides are not affected. The filtrate may be treated gravimetrically or volumetrically (Wilner).

Proportional Weights of Equivalent Quantities of Iron and its Salts.

Metal	Fe_2	112
Ferric oxide	Fe_2O_3.	160
Ferric hydrate.	Fe_26HO	214
Ferric chloride	Fe_2Cl_6	324·4
Ferric sulphate	Fe_23SO_4.	400
Ferrous sulphate	$2(FeSO_4,7H_2O)$	556

ARSENIUM.

Arsenic (As_2O_3) is usually estimated volumetrically (*vide* p. 762), and sometimes arseniates also (*vide* p. 734), but the latter are best precipitated as a lead salt; an "aqueous solution of 12·4 grains of anhydrous arseniate of sodium, acidulated with acetic acid, requires not less than 34 grains of acetate of lead for complete precipitation." With certain precautions arsenium may be precipitated and weighed as sulphide (As_2S_3).

Process 1.—The pure, white arsenic in lump (about 0·2) is dissolved in a flask in a small quantity of water containing bicarbonate of sodium or potassium, the liquid being heated. A slight excess of hydrochloric acid is then added, and sulphuretted hydrogen gas passed through the solution so long as a precipitate falls, the mouth of the flask being stopped by a plug of cotton-wool (to prevent undue access of air and consequent decomposition of the gas, resulting in precipitation of sulphur). The mixture is warmed in the flask and carbonic acid gas passed through it until the odour of sulphuretted hydrogen has nearly disappeared; the precipitate is collected on a tared filter, washed as quickly as possible with hot water containing a little sulphuretted hydrogen, dried in a water-oven, and weighed. 198 parts of arsenic should yield 246 of sulphide of arsenium.

Process 2.—The arsenium must be present in the arsenic condition. If the operator is not certain that this is the case, the solution must be warmed with a little hydrochloric acid and a few grains of chlorate of potassium added until a distinct odour of chlorous vapour is evolved—which is then allowed to escape by continued application of heat. To the solution thus obtained ammonia, which must produce no turbidity, is added in excess, and then magnesia mixture (*see* under "phosphates," p. 803). The solution is set aside for 24 or 48 hours. The precipitate is collected on a filter and washed with as little ammonia water (1 to 3) as possible until the filtrate ceases to give a reaction for chlorides. The precipitate is then dried on the filter, the precipitate and filter-paper burned, and the whole gently ignited in a crucible, and weighed. This residue is pyroarseniate of sodium and has the formula $Mg_2As_2O_7$.

ANTIMONY.

The metal is precipitated in the form of sulphide (Sb_2S_3), with the precautions observed in estimating arsenium—a small quantity of tartaric acid, as well as hydrochloric, being added to prevent the precipitation of an oxysalt. If the sulphuretted hydrogen be passed through a *hot* solution, the particles of precipitate aggregate better and the latter may be more quickly filtered out and washed. The experiment may be performed on about half a gramme of pure tartar-emetic; the salt should yield nearly half its weight of sulphide. According to Fresenius, the sulphide dried at 100° C. still contains 2 per cent. of water, and must be heated in a current of carbonic acid gas, until it turns from an orange to a black colour, before all moisture is expelled. In the British Pharmacopœia the purity of tartar-emetic (*Anti-*

monium Tartaratum), and the strength of solution of chloride of antimony (*Liquor Antimonii Chloridi*), are determined by the above process. Of the *Antimonium Sulphuratum*, B.P., it is stated "that sixty grains moistened and warmed with successive portions of nitric acid until red fumes cease to be evolved, and then dried and heated to redness, give a white residue [Sb_2O_4] weighing about 40 grains."

For the volumetric estimation of antimony in antimonious salts, *see* p. 763.

COPPER.

Copper is precipitated from its solutions and weighed either (1) as metal (Cu_2), or (2) as oxide (CuO).

Process 1.—Dissolve about half a gramme of dry crystallized sulphate of copper in a small quantity of water, in a tared porcelain crucible or breaker, acidulate with hydrochloric acid, introduce a fragment or two of pure zinc, cover the vessel with a watch-glass, and set aside till evolution of hydrogen has ceased and the still acid liquid is colourless. The copper is then washed with hot water by decantation until no trace of acid remains, the precipitate drained, rinsed with strong spirit of wine, dried in the water-oven, cooled, and weighed.

Process 2.—From a solution acidulated by sulphuric acid and placed in a platinum crucible copper may be entiroly deposited in a coherent form by a weak current of electricity, the crucible being connected with tho zinc pole of the battery, a platinum spatula suspended in the solution forming the positive pole. The crucible may afterwards be freed from the deposited copper by nitric acid.

Process 3.—About three-fourths of a gramme of sulphate of copper is accurately weighed, dissolved in half a litre of water, the liquid boiled; dilute solution of potash or soda is then added till no more precipitate falls, ebullition continued for a short time, and the beaker set aside; the supernatant liquid is decanted, the precipitate boiled with water twice or thrice, collected on a filter, washed, dried, transferred to a crucible, the filter incinerated, and its ash moistened with a drop of nitric acid; the whole is finally heated strongly, cooled, and weighed.

249·3 parts of sulphate of copper yield 79·3 of oxide, or 63·3 of metal.

Other Processes.—Vide Pharmaceutical Journal for April 3, 1880, p. 801.

BISMUTH.

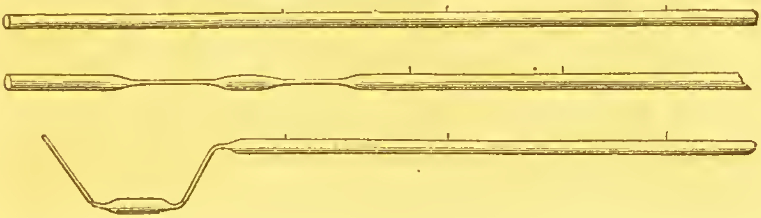
Dissolve 0·3 or 0·4 of the pure oxycarbonate of bismuth $(Bi_2O_2CO_3)_2,H_2O$ (*Bismuthi Carbonas*, B.P.) in a very small quantity of hydrochloric acid, dilute with water slightly acidulated by hydrochloric acid, pass excess of sulphuretted hydrogen through the liquid, collect the precipitate on a tared filter, wash, dry at 100° C., and weigh. The sulphide must not be exposed too long in the water-oven, or it will increase in weight owing to absorption of oxygen; hence it should be tested in the balance every half-hour during desiccation. 519 of oxycarbonate should yield 514 of sulphide (Bi_2S_3). The strength of the official solution of citrate of bismuth and ammonium (*Liquor Bismuthi et Ammonii Citratis*, B.P.) is determined by this process. "Two fluid drachms of the solution, mixed with an ounce of distilled water, and treated with sulphuretted hydrogen in excess, yield a black precipitate, which, collected, washed, and dried, weighs about seven grains. One fluid drachm yields three grains of oxide of bismuth." Of the official Citrate of Bismuth, B.P., it is stated that "ten grains dissolved in solution of ammonia and treated with sulphuretted hydrogen in excess, yield a precipitate which, when washed and dried, weighs about seven grains;" and of the Citrate of Bismuth and Ammonium, B.P., "ten grains dissolved in water and treated with sulphuretted hydrogen in excess, yield a precipitate which, when washed and dried, weighs about six and a half grains." The atomic weight of bismuth is 208 if oxygen = 16, or 207·5 if oxygen = 15·96.

MERCURY.

This element may be (1) isolated and estimated in the form of metal, or precipitated and weighed as (2) mercurous chloride, or (3) mercuric sulphide.

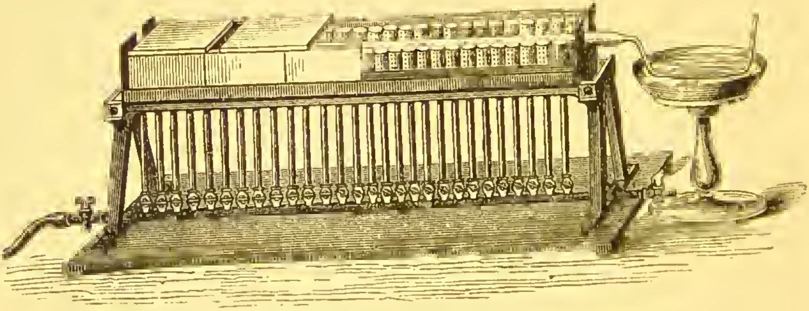
Process 1.—The process by which the metal itself is separated is one of distillation into a bulb surrounded by water. About half a mètre of the difficultly fusible German glass known as *combustion-tubing* is sealed at one end after the manner of a test-tube (fig. 79); a mixture of bicarbonate of sodium and dry chalk is then dropped into the tube to the height of two or three centimètres, and, next, several small fragments of quicklime so as to occupy another centimètre; a mixture of about a gramme of pure calomel or corrosive sublimate with enough powdered quicklime to occupy 10 or 12 centimètres of the tube is added, then the lime-rinsings of the mixing-mortar, a layer of a few centimètres of powdered quicklime, and, finally, a plug of *asbestos*. The whole should occupy two-thirds of the tube. The part of the tube just above the asbestos is now softened in the blowpipe-flame and drawn out about a décimètre to the diameter of a narrow quill (fig. 80); again drawn out to the same extent at a point two or three centimètres nearer the mouth (fig. 80) and any excess of tubing cut off. The bulb thus formed may be enlarged by softening and blowing. The tube is next softened at a point close to but anterior to the asbestos, and bent to form an obtuse angle; the tubo is then softened close to the bulb and slightly bent so that the bulb may be parallel with the large tube; then softoned on the other sido

Figs. 79, 80, 81.



of the bulb, and the terminal tube bent to an obtuse angle, so that, the tube being held in a horizontal position, the bulb may be sunk in water, and the terminal tube point upwards (fig. 81). The long tube is now laid in the gas-furnace found in most laboratories (fig. 82), a basin so placed that the bulb of the apparatus may be cooled by being surrounded by water, the part of the tube occupied by asbestos heated to redness, and the flame slowly lengthened until the whole tube is red-hot. Under the circumstances just described the mercurial compound volatilizes, is decomposed by the lime, and its acidulous radical fixed, the mercury carried in vapour to and condensed in the bulb, the carbonic acid gas evolved from the bicarbonate of sodium and chalk washing out the last portions of mercury-vapour from the tube. When the distillation is considered to be complete, the dish of water is removed, the bulb dried, and then detached by help of a file at a point beyond any sublimate of mercury. The dried bulb is weighed, the mercury shaken or dissolved out, and the tube again dried and weighed. The difference between the weights gives the weight of the mercury. "Ammoniated Mercury," B.P., should yield, theoretically, 79·52 per cent., practically about 77·5 per cent., of metallic mercury.

Fig. 82.



DISTILLATION OF MERCURY FOR QUANTITATIVE PURPOSES.

Process 2.—The process by which mercury is separated in the form of calomel, consists in adding solution of hydrochloric and of phosphorous acids to an aqueous or even acid solution of a weighed quantity of the mercurial compound, setting the mixture aside for twelve hours, collecting the precipitate on a tared filter, washing, drying at 100° C., and weighing (Rose). The experiment may be tried on half a gramme to a gramme of corrosive sublimate.

Process 3.—Two or three décigrammes of corrosive sublimate are dissolved in water, the solution acidulated with hydrochloric acid, excess of sulphuretted hydrogen passed through it, the precipitate collected on a tared filter, washed with cold water, dried at 100° C., and weighed.

Proportional Weights of Equivalent Quantities of Mercury and its Salts.

Metal	Hg.	200
Mercurous chloride	$HgCl$	235·4
Mercuric chloride	$HgCl_2$.	270·8
Mercuric sulphide	HgS	232

LEAD.

Lead is generally estimated either as (1) oxide, (2) sulphate, (3) chromate, or (4) metal.

Process 1.—Weigh out one or two grammes of pure acetate of lead in a covered crucible, previously tared, and heat slowly until no more vapours are evolved. Remove the lid, stir down the carbonaceous mass with a clean iron wire, and keep the crucible in the flame so long as any carbon remains unconsumed. Introduce some fragments of fused nitrate of ammonium, and again ignite until no metallic lead remains and all excess of the nitrate has been decomposed. Cool and weigh the resulting oxide (PbO).

Process 2.—Dissolve 0·4 or 0·5 of a gramme of acetate of lead in a small quantity of water, drop in diluted sulphuric acid, add to the mixture twice its bulk of methylated spirit of wine, and set aside. Decant the supernatant liquid, collect the sulphate on a filter, wash with spirit, dry, transfer to a porcelain crucible, removing as much of the sulphate as possible from the paper, incinerate on the crucible-lid (not in the platinum coil, for the fused particles of reduced lead would alloy with the platinum), ignite, cool, and weigh.

Process 3.—About half a gramme of acetate of lead is dissolved in two or three hundred c.c. of water, acetic acid added, and then solution of red chromate of potassium. Collect the precipitate on a tared filter, wash, dry at 100° C., and weigh.

Process 4.—In certain cases, notably in that of commercial "white load," the lead may be estimated in the metallic state by means of cyanide of potassium. The lead paint (about 20 grammes) is weighed and carefully incinerated. The residue, a mixture of metallic lead and oxide of lead, is then mixed with several times its bulk of cyanide of potassium and the whole heated to fusion. With careful manipulation the lead collects in one globule, which, after cooling, may readily be separated from the mixed cyanide and cyanate and weighed. Commercially pure white lead should yield 74 per cent. of lead.

Proportional Weights of Equivalent Quantities of Lead and its Salts.

Metal	Pb	206·4
Acetate	$Pb2C_2H_3O_2, 2H_2O$	378·4
Oxide	PbO	222·4
Sulphate	$PbSO_4$	302·4
Chromate	$PbCrO_4$	322·9

SILVER.

Compounds of silver which are readily decomposed by heat are estimated in the form of (1) metal, others usually as (2) chloride ($AgCl$), but sometimes as (3) cyanide ($AgCN$).

Process 1.—Heat about a gramme of oxide of silver (Ag_2O) in a tared crucible, cool, and weigh. 232 of oxide yield 216 of metal. "29 grains heated to redness yield 27 grains of metallic silver."—*Brit. Pharm.*

Process 2.—Dissolve 0·4 or 0·5 of pure dry crystals of nitrate of silver in water, acidulate with two or three drops of nitric acid, slowly add hydrochloric acid, stirring rapidly, until no more precipitate falls. Pour off the supernatant liquid through a filter, wash the chloride of silver once or twice with hot water, transfer to the filter, complete the washing, and dry. After removing as much as possible of the precipitate from the paper to the crucible, burn the filter, not in a wire helix but on the inverted lid of the crucible, moisten with a drop of nitric acid, warm, add a drop of hydrochloric acid, evaporate to dryness, replace the lid on the crucible, ignite the whole until the edges of the mass of chloride begin to fuse; cool, and weigh. 170 of nitrate yield 143·4 of chloride. According to the British Pharmacopœia, 10 parts of nitrate should thus yield 8·44 of chloride, and the filtrate from the chloride evaporated to dryness should leave no residue, indicating absence of nitrates of potassium or sodium and other similar foreign substances. 30 parts of "Mitigated Caustic" (*Argenti et Potassii Nitras*, B.P.), similarly treated, give 8·44 parts of chloride of silver, and the filtrate yields nitrate and chloride of potassium on evaporation. "Toughened Caustic," B.P., contains 5 per cent. of nitrate of potassium, hence 10 parts will give only 8 parts of chloride of silver, and the filtrate will yield a little potassium salt. 10 of silver, if pure (*Argentum Purificatum*, B.P.), will give 13·285 of chloride of silver.

Process 3.—Cyanide of silver may be collected on a tared filter and dried at 100° C. 170 of nitrate yield 134 of cyanide. Silver and its salts may be volumetrically estimated by a standard solution of chloride of sodium.

Cupellation.—The amount of silver in an alloy may also be determined by a dry method. The metal is folded in a piece of thin sheet lead, placed on a *cupel* (*cupella*, little cup, made of compressed bone-earth) and heated in a furnace, the cupel being protected from the direct action of the flame by a muff-shaped or, rather, oven-shaped case, termed a muffle. The metals melt, the baser become oxidized, the oxide of lead fusing and dissolving the other oxides; the fluid oxides are absorbed by the porous cupel, a button of pure silver remaining. An alloy suspected to contain 95 per cent. of silver requires about three times its weight of lead for successful cupellation; if 92½ per cent. (English silver coin), between five and six times its weight of lead is necessary.

QUESTIONS AND EXERCISES.

Explain the gravimetric process by which the strength of the officia solutions of ferric chloride, nitrate, and sulphate are determined.—Mention the various amounts of ferrous and ferric salts equivalent to 100 parts of metal.—State the precautions necessary to be observed in esti mating arsenium or antimony in the form of sulphide.—In what form are the official compounds of bismuth weighed for quantitative purposes?—Give an outline of the process by which mercury may be isolated from its official preparations and weighed in the metallic condition.—Describe three methods for the quantitative analysis of salts of lead; and the weights of the respective precipitates, supposing 0·56 of crystallized acetate to have been operated on in each case.—Describe the processes by which silver is estimated in the forms of metal, chloride, and cyanide.—What proportions of nitrate of silver are indicated, respectively, by 15 of metal, 9·8 of chloride, and 8·1 of cyanide?—Describe cupellation.

GRAVIMETRIC ESTIMATION OF THE ACIDULOUS RADICALS OF SALTS.

CHLORIDES.

Free chlorine (chlorine-water) and compounds which by action of acids yield free chlorine (Chlorinated Lime, Chlorinated Soda, and their official Solutions) are estimated volumetrically by a standard solution of hyposulphite of sodium (*vide* p. 769). The amount of combined chlorine in pure chlorides (HCl,NaCl) may also be determined by volumetric analysis with a standard solution of nitrate of silver (p. 755).

Combined chlorine is gravimetrically estimated in the form of chloride of silver, the operation being identical with that just described for silver salts (p. 792). 58·4 parts of pure, colourless, crystallized chloride of sodium (rock-salt) yield 143·4 of chloride of silver.

IODIDES.

Free iodine is estimated volumetrically by solution of hyposulphite of sodium (*vide* p. 769).

Combined iodine is determined gravimetrically in the form of iodide of silver, the operations being conducted as with chloride of silver. Iodide of potassium may be used for an experimental determination: KI=166 should yield AgI=235. Of the iodide of cadmium (*Cadmii Iodidum*, B.P., 1867) it is stated that "ten grains dissolved in water, and nitrate of silver added in excess, give a precipitate which, when washed with water and afterwards with half an ounce of solution of ammonia, and dried, weighs 12·5 grains."

In presence of chlorides and bromides the iodine in iodides may be precipitated and weighed as iodide of palladium.

Moisture in iodine is estimated by loss on exposing a weighed quantity of iodine in a capsule over a dish of sulphuric acid under a small bell jar; or by adding to a weighed sample five or six times as much mercury, or twice as much zinc, and a little water, drying and weighing. The product is the amount of metal employed plus that of the *dry* iodine in the sample.

BROMIDES.

Free bromine may be estimated by shaking with excess of solution of iodide of potassium, and then determining the equivalent quantity of liberated iodine by a standard solution of hyposulphite of sodium (p. 769).

The bromine in bromides may be precipitated and weighed as bromide of silver, the manipulations being the same as those for chloride of silver: 0·2 to 0·3 of pure bromide of potassium may be used for an experimental analysis.

CYANIDES.

The hydrogen cyanide (hydrocyanic acid) is usually estimated volumetrically (*vide* p. 756).

From all soluble cyanides cyanogen may be precipitated by nitrate of silver, after acidulating with nitric acid, the cyanide of silver being collected on a tared filter, dried at 100° C., and weighed.

Of the official Diluted Hydrocyanic Acid, it is stated that one hundred grains (or 110 minims) precipitated by solution of nitrate of silver yield ten grains of dry cyanide of silver.

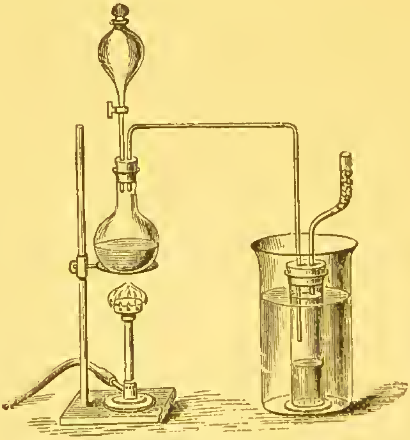
Cyanide of Silver.

		In 1 molec. wt.	In 100 parts.
Silver	Ag	107·66	80·55
Cyanogen	CN	26·00	19·45
		133·66	100·00

NITRATES.

Nitrates cannot be estimated by direct gravimetric analysis, none of the basylous radicals yielding a definite nitrate insoluble in water. With some difficulty they may be determined by indirect volumetric methods.

Fig. 83.



ESTIMATION OF NITRATES.

Process.—The following (Thorpe's) method depends upon the fact (Gladstone and Tribe) that when zinc upon which copper is deposited in a spongy form is boiled with water, hydrogen is evolved. Thorpe found that in a solution containing nitrates the nascent hydrogen converts the whole of the nitrogen of the nitrates into ammonia, which may be collected and estimated. (The oxygen of the nitrate is simultaneously converted into water, the nitrate-metal into hydrate, and the zinc into hydrate of zinc. The power of the copper-zinc couple is considered to depend largely on the hydrogen absorbed by the finely divided metal.)

An apparatus such as shown in fig. 83 should be constructed. A flask (about 100 c.c.) is fitted with a clean sound cork perforated for a delivery-tube, which should be of strong glass tubing of about a quarter-inch bore, and for a stoppered funnel, which should have about half the capacity of the flask. The whole is supported by a clamp or on wire-gauze. The outer jar shown in the figure should have a capacity of two or three litres, and the inner receiving-jar should be capable of holding 200 c.c. The latter is fitted with a cork perforated for the delivery-tube, and perhaps for another tube containing fragments of glass moistened with acidulated water to prevent possible loss of ammonia—though the latter tube is practically found to be almost unnecessary. The addition of washing-bottle tubes is also recommended as convenient for obtaining the distillate from the jar without dismounting the apparatus from time to time.

A few strips of clean zinc (*granulated* zinc recently cleansed with diluted acid is best), are boiled in a beaker with a three per cent. solution of sulphate of copper, the operation being repeated with a fresh portion of solution until an adherent and fairly thick coating of finely divided copper is deposited. The pieces of metal are well washed and introduced into the flask which is then half filled with pure water free from ammonia. To avoid transference, the flask itself may be used instead of the beaker. The funnel also of the apparatus is filled with pure water. Water is now placed around the inner receiver in the outer jar, and, the connections being sound, heat is applied with the view of freeing the apparatus itself from any trace of ammonia. When the contents of the flask are evaporated nearly to dryness, pure water is admitted from the funnel until the flask is again about half full (the funnel should be filled again at once), and the distillation carried on as before. This must be repeated until no further trace of ammonia is evolved, when the apparatus is ready for use. On each occasion that the apparatus is used it must be freed from ammonia in this way. A suitable quantity of the substance to be estimated is now introduced (in the case of potable waters the prepared solid residue from 100 c.c.) and water added, if necessary, until the flask is half full. Heat is now applied and the operation conducted in the manner already described until ammonia ceases to come over—a point which usually occurs in the case of water-residues when the flask has been twice or thrice charged with water and the distillate is about 100 c.c. The warm water from the upper part of the cooling-jar may be removed by a siphon or otherwise, cold water being introduced from time to time.

The ammonia being all evolved, disconnect the flask and receiver simultaneously (unless washing-bottle tubes are fitted), and treat the contents of the latter by the Nessler method described on page 745.——Urea yields but traces of ammonia by this process; and neither the sulphates nor chlorides of the alkali-metals affect the result.——The method is only applicable to highly dilute solutions of nitrates, for with stronger solutions oxides of nitrogen are formed and escape.

SULPHIDES.

Process 1.—Soluble sulphides (H_2S,NaHS, *e.g.*) may be estimated volumetrically by adding to the aqueous liquid a measured excess of an alkaline solution of arsenic of known strength, neutralizing by hydrochloric acid, diluting to any given volume, filtering off the sulphide of arsenium precipitated, taking a portion of the filtrate equal to a half or a third of the original volume, and, after neutralizing by acid carbonate of sodium, estimating the residual arsenic by the standard iodine solution (*vide* p. 762). The process may be tried on a measured volume of sulphuretted hydrogen (the weight of which is easily calculated; 1 litre of hydrogen = 0·0896 gramme) absorbed by a strong solution of soda or potash.

Process 2.—Sulphur and sulphides may also be quantitatively analysed by oxidizing to sulphuric acid and precipitating in the form of sulphate of barium. A couple of décigrammes of a pure metallic sulphide may be decomposed by careful deflagration with a mixture of chlorate of potassium and carbonate of sodium, the product dissolved in water, acidulated with hydrochloric acid, solution of chloride of barium added, and the precipitated sulphate of barium washed and collected as described in connection with the estimation of barium (p. 779). Many sulphides may be oxidized in a flask by chlorate of potassium and hydrochloric acid, and then precipitated by chloride of barium. Experimental determinations may also be made on a weighed fragment of sulphur, about 0·1, cautiously fused with a little solid caustic alkali, and the product oxidized while hot by the slow addition of powdered nitrate or chlorate of potassium, or, when cold, by treatment with chlorate of potassium and hydrochloric acid, and subsequent precipitation by chloride of barium.

Note.—Fusions performed by help of a gas-lamp must be carefully conducted; for any alkali that may creep over the side of a crucible will certainly absorb sulphurous acid from the products of combustion of the gas, and error result.

Process 3.—Soluble sulphides may also be treated with excess of an alkaline arsenite, arsenious sulphide then be precipitated by the addition of hydrochloric acid, and the precipitate collected and weighed with the usual precautions (*vide* p. 785).

Weights of Equivalent Quantities of Sulphur and its Compounds.

Sulphur	S	32
Sulphuretted hydrogen	H_2S	34
Sulphate of barium	$BaSO_4$	232·8
Arsenious sulphide	$(As_2S_3) \div 3$	82
Bisulphide of iron.	$(FeS_2) \div 2$	60
Sulphide of lead	PbS	238·4

SULPHITES.

Sulphites are usually estimated volumetrically by a standard solution of iodine (*vide* p. 761). Sulphites insoluble in water are diffused in that menstruum, hydrochloric acid added, and the iodine solution then dropped in.

If necessary, sulphites may be estimated gravimetrically by oxidation and precipitation as sulphate of barium.

SULPHATES.

These salts are always precipitated and weighed as sulphate of barium, the manipulations being identical with those performed in the determination of barium by means of sulphates (*vide* p. 778). The purity of Sulphate of Sodium (*Sodii Sulphas*, B.P.), and the presence of not more than a given amount of sulphuric acid in Vinegar (*Acetum*, B.P.), are directed, in the British Pharmacopœia, to be ascertained by this process. Ten grains of sulphate of sodium yield 7·23 of sulphate of barium. Five ounces of vinegar should yield not more than about one-third of a gramme of sulphate of barium.

Sulphates may be estimated volumetrically by a seminormal solution of pure chloride of barium, $BaCl_2,2H_2O = 244$.

The amount of free sulphuric acid or hydrochloric acid in vinegar, lemon juice, lime juice, etc., may also be ascertained volumetrically by adding a known quantity of standard solution of soda, evaporating to dryness, incinerating, dissolving in water, and by standard acid estimating the quantity of soda still remaining free. The soda lost indicates the amount of free mineral acid (Hehner). Thresh first estimates the chlorine in a sample of vinegar, then adds a known additional amount of chlorine, preferably in the form of chloride of barium, evaporates, ignites, treats with water, adds bicarbonate of sodium to remove excess of barium, filters, and again estimates the chlorine. A loss of 70·8 of chlorine (Cl_2) indicates 98 of *free* sulphuric acid (H_2SO_4).

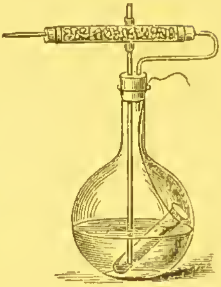
The method of estimating free sulphuric, nitric, or hydrochloric acids, proposed by Spence and Esilman, is founded on their power of decolorizing a standard solution of ferric acetate.

Proportional Weights of Equivalent Quantities of Sulphates.

The sulphuric radical . .	SO_4	96
Sulphuric acid	H_2SO_4	98
Sulphate of barium . .	$BaSO_4$	232·8

CARBONATES.

Fig. 84.



ESTIMATION OF CARBONATES.

Carbonates are usually estimated by the loss in weight they undergo on the addition of a strong acid.

Process 1.—A small light flask is selected—of such a size that it can be conveniently weighed in a delicate balance. Two narrow glass tubes are fitted to the flask by a cork—the one straight, extending from about two or three centimètres above the cork to the bottom of the flask, the other cut off close to the cork on the inside and curved outwards so as to carry a thin drying-tube horizontally above the flask (*see* fig. 84). The drying-tube is nearly filled with small pieces of chloride of calcium, a plug of cotton-wool preventing escape of any fragments at either end, and is attached by a pierced cork to the free extremity of the curved tube of the flask. A weighed quantity of any pure soluble carbonate is placed in the flask, a little water added, a miniature test-tube containing sulphuric acid lowered into the flask by a thread and supported so that the acid may not flow out, the cork inserted, the outer end of the piece of the straight glass tubing closed by a cap or a fragment of cork, and the whole weighed. The apparatus is then inclined so that the sulphuric acid and carbonate may slowly react; carbonic acid gas is evolved and escapes through the horizontal tube, any moisture being retained by the chloride of calcium. When effervescence has ceased, the gas still remaining in the vessel is sucked out; this is accomplished by adapting a piece of india-rubber tubing to the end of the drying-tube, removing the small plug from the straight tube, and aspirating slowly with the mouth for a few minutes. If the heat produced by the action of the sulphuric acid and solution is considered insufficient to expel all the carbonic acid from the liquid, the plug is again inserted in the tube and the contents of the flask gently boiled for some seconds. When the apparatus is nearly cold, more air is again drawn through it, and the whole finally weighed. The loss is due to carbonic acid gas (CO_2), from the weight of which that of any carbonate is ascertained by calculation. Carbonates insoluble in water may be attacked by hydrochloric instead of sulphuric acid; granulated mixtures of carbonates and powdered tartaric or citric acids by enclosing the preparation in the inner tube and placing water in the flask, or *vice versâ*. The apparatus also may be modified in many ways to suit the requirements, convenience, or practice of the operator.

Process 2.—Carbonates from which carbonic acid gas is evolved by heat may be estimated by the loss they experience on ignition.

Process 3.—Free carbonic acid gas may be absorbed by a solid stick of potash or strong alkaline solution, the loss in volume of the gas or mixture of gases indicating the amount originally present.

Weights of Equivalent Quantities of Carbonic Acid Gas and certain Carbonates.

Carbonic acid gas	CO_2	44
Carbonic acid.	H_2CO_3 . . .	62
Anhydrous carbonate of sodium .	Na_2CO_3 . . .	106
Crystalline carbonate of sodium .	$Na_2CO_3,10H_2O$	286
Anhydrous carbonate of potassium.	K_2CO_3 . . .	138
Crystalline carbonate of potassium	$K_2CO_3+16\%Aq$	164·285
Carbonate of calcium	$CaCO_3$ . . .	100

OXALATES.

Process 1.—The oxalic radical is usually precipitated in the form of oxalate of calcium, and weighed as carbonate, the manipulations being identical with those observed in the estimation of calcium (*vide* p. 780). The experiment may be performed on 0·3 or 0·4 of a gramme of pure oxalic acid, 126 parts of which should yield 100 of carbonate of calcium.

Process 2.—Oxalates may also be determined by conversion of their acidulous radical into carbonic acid gas, and observation of the weight of the latter. The oxalate, water, and excess of black oxide of manganese are placed in the carbonic-acid apparatus (p. 801), a tube containing sulphuric acid lowered into the flask, the whole weighed, and the operation completed as for carbonates. From the following equation it will be seen that every 88 parts of carbonic acid gas evolved indicates the presence of 126 parts of crystallized oxalic acid or an equivalent quantity of other oxalate :—

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2$$

The black oxide of manganese used in this experiment must be free from carbonates. The amount of materials employed is regulated by the size of the vessels.

PHOSPHATES.

Process 1.—*From phosphates dissolved in water* the phosphoric radical may be precipitated and weighed in the form of pyrophosphate of magnesium, the details of manipulation being similar to those observed in estimating magnesium (*vide* p. 781). Half a gramme or rather more of pure dry crystallized phosphate of sodium may be employed in experimental determinations. The official phosphate of ammonium (*Ammonii Phosphas*, B.P.) is quantitatively analysed by this method. "If twenty grains of this salt be dissolved in water, and solution of ammonio-sulphate of magnesium be added, a crystalline precipitate falls, which, when well washed upon a filter with solution of ammonia diluted with an equal volume of water, dried, and heated to redness, leaves 16·8 grains." Half a gramme, or less, is a more convenient quantity if the operations be conducted with care. *Solution of ammonio-sulphate of magnesium* (B.P.) is prepared by dissolving 2 parts of sulphate of magnesium, 1 of chloride of ammonium, and 1 of solution of ammonia (20·6 per cent. NH_4HO) in 18 or 20 of distilled water; such a solution is of considerable use if several phosphoric determinations are about to be made.

Process 2.—*Free phosphoric acid* is most readily determined as phosphate of lead (Pb_32PO_4). Of the official (B.P.)

diluted phosphoric acid it is stated that "355 grains by weight (or 73·8 of the official 'concentrated' acid) poured upon 180 grains of oxide of lead in fine powder leave, by evaporation, a residue (principally phosphate of lead) which after it has been heated to dull redness, weighs 215·5 grains." One-tenth of these quantities may be used for experimental purposes; one to two grammes will give good results. The oxide of lead must be quite pure; it should be prepared by digesting red lead in warm diluted nitric acid, washing, drying, and heating the resulting puce-coloured plumbic oxide in a covered porcelain crucible. The increase in weight obtained on evaporating a given amount of solution of phosphoric acid with a known weight of perfectly pure oxide of lead (PbO) may be regarded as entirely due to phosphoric anhydride (P_2O_5); $3PbO + P_2O_5 = Pb_32PO_4$, the actual reaction being $3PbO + 2H_3PO_4 = Pb_32PO_4 + 3H_2O$. From these equations, and the atomic weights (*vide* Appendix or Table on next page), the percentage of phosphoric acid (H_3PO_4) in any specimen of its solution may easily be calculated.

Process 3.—*The strength of pure solution of phosphoric acid.* This is by specific gravity and reference to Tables.

Process 4.—Bone earth, "superphosphate," the official *Calcii Phosphas*, and other forms of phosphate of calcium known to be tolerably free from iron or aluminium, may be estimated by treating about half a gramme with hydrochloric acid somewhat diluted, filtering, if necessary, warming, precipitating with excess of ammonia, collecting the precipitate (Ca_32PO_4), washing, drying, igniting and weighing. The phosphate of calcium of pharmacy (*Calcii Phosphas*, B.P.), if pure, will in this process lose little or no weight.

Process 5.—*Insoluble phosphates* in ashes, manures, etc., are treated as follows. The weighed material (1·0 to 10·0 grammes) is digested in hydrochloric acid diluted with three or four times its bulk of water, filtered (insoluble matter and filter being thoroughly exhausted by water), ammonia added to the filtrate and washings, until, after stirring, a faint cloudy precipitate is perceptible, solution of oxalic acid dropped in until, after agitation for a few minutes, the opalescence is destroyed, oxalate of ammonium next added, the whole warmed, oxalate of calcium removed by filtration, and the filtrate concentrated if very dilute, the liquid treated with citric acid in such quantity that ammonia when added in excess gives a clear *lemon-yellow* solution (Warington), magnesian mixture poured in (as in process 1), and the precipitate of ammonio-magnesian phosphate collected, washed, dried, and weighed, as already described in connection with the estimation of magnesium.

Relative Weights of Equivalent Quantities of Phosphoric Compounds.

Phosphoric acid	H_3PO_4		98
Pyrophosphate of magnesium .	($Mg_2P_2O_7$ = 222)	÷ 2 =	111
Phosphate of lead	(Pb_32PO_4 = 809·2)	÷ 2 =	404·6
Phosphoric anhydride . . .	(P_2O_5 = 142)	÷ 2 =	71
Phosphate of calcium . . .	(Ca_32PO_4 = 310)	÷ 2 =	155
Superphosphate of calcium .	(CaH_42PO_4 = 234)	÷ 2 =	117

QUESTIONS AND EXERCISES.

What quantity of pure rock-salt is equivalent to 4·2 parts of chloride of silver? *Ans.*, 1·71.—State the percentage of real iodide of potassium contained in a sample of which 8 parts yield 10·9 of iodide of silver. *Ans.*, 96·25.—What is the strength of a solution of hydrocyanic acid 10 parts of which, by weight, yield 0·9 of cyanide of silver? *Ans.*, 1·81 per cent.—How are nitrates quantitatively estimated?—By what processes may the strength of sulphides be determined?—How much real sulphate of sodium is contained in a specimen 10 parts of which yield 14·2 of sulphate of barium? *Ans.*, 86·61 per cent.—Give details of the operations performed in the quantitative analysis of carbonates.—What amount of carbonic acid gas should be obtained from 10 parts of acid carbonate (or bicarbonate) of potassium? *Ans.*, 4·4 parts.—To what operation and what proportions of materials does the following equation refer?

$$Na_2C_2O_4 + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2.$$

Explain the lead process for the estimation of phosphoric acid in the official solution.—State the amount of superphosphate of calcium equivalent to 7·6 parts of pyrophosphate of magnesium. *Ans.*, 8·01 parts.

SILICATES.

Silica (SiO_2) may be separated from alkaline silicates, or from silicates decomposable by hydrochloric acid, by digesting the substance in hydrochloric acid at a temperature of 70° to 80° C. until completely disintegrated, evaporating to dryness, heating in an air-bath, again moistening with acid, diluting with hot water, filtering, washing, drying, igniting, and weighing.

ESTIMATION OF WATER.

Water and other matters readily volatilized are most usually estimated by the loss in weight which a substance undergoes on being heated to a proper temperature. Thus, in the British Pharmacopœia, crystalline gallic acid ($H_3C_7H_3O_5, H_2O$) is stated to lose 9·5 per cent. of its weight at a temperature of 100° C., oxalate of cerium ($Ce_23C_2O_4,9H_2O$) 52 per cent. on incineration, carbonate of potassium about 16 per cent. on exposure to a red heat, sulphate of quinine ($2C_{20}H_{24}N_2O_2,H_2SO_4,7H_2O$) 15·2 per cent. at 100° C., arseniate of sodium ($Na_2HAsO_4,7H_2O$) 40·38 per cent. at 149° C., carbonate of sodium ($Na_2CO_3,10H_2O$) 62·94 per cent., phosphate of sodium ($Na_2HPO_4,12H_2O$) 63 per cent., and sulphate of sodium ($Na_2SO_4,10H_2O$) 55·9 per cent. at a low red heat: oxide of bismuth heated to incipient redness is not to diminish in weight. Ferric oxyhydrate " yields about 10 per cent. of moisture."

Process.—One or two grammes of substance is sufficient in experiments on desiccation, the material being placed in a watch-glass, covered or uncovered porcelain crucible, or other vessel, according to the temperature to which it is to be exposed.

Rapid desiccation at an exact temperature may be effected by introducing the substance into a tube having somewhat the shape of the letter U, sinking the lower part of the tube into a liquid kept at a definite temperature by aid of a thermometer, and drawing or forcing a current of dry air slowly through the apparatus. Substances liable to oxidation may be desiccated in a current of dried carbonic acid gas. The weights of the U-tube before and after the introduction of the salt, and after desiccation, give the amount of water sought. In all cases the material must be heated until it ceases to lose weight. Occasionally it is desirable to estimate water directly by conveying its vapour in a current of air through a weighed tube containing chloride of calcium and re-weighing the tube at the close of the operation; the increase shows the amount of water.

Note.—Highly dried substances rapidly absorb moisture from the air; they must therefore be weighed quickly, enclosed, if possible, in tubes (p. 748), a pair of clamped watch-glasses, or a crucible having a tightly fitting lid.

CARBON, HYDROGEN, OXYGEN, NITROGEN.

The quantitative analysis of animal and vegetable substances is either *proximate* or *ultimate.*

Proximate Quantitative Analysis includes the estimation of water, oil, albumen, starch, cellulose, gum, resin, alkaloids, acids, glucosides, ash. It requires the application of much theoretical knowledge and manipulative skill, and cannot well be studied except under the guidance of a tutor. One of the best works on the subject is by Rochleder, a translation of whose monographs will be found in the *Pharmaceutical Journal*, vol. i., 2nd ser., pp. 562, 610; vol. ii., 2nd ser., pp. 24, 129, 160, 215, 274, 420, 478. Another is by Prescott, "Outlines of Proximate Organic Analysis." The fullest is by Dragendorff, translated by H. G. Greenish, "Plant Analysis."

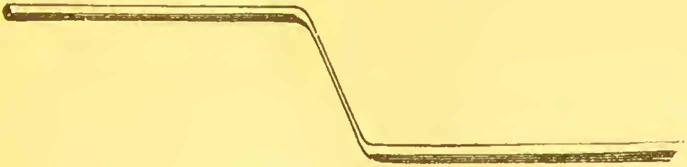
Ultimate Quantitative Organic Analysis can only be successfully accomplished with the appliances of a well-appointed laboratory—a good balance, a gas-furnace (p. 790) giving a smokeless flame (7 or 8 centimètres wide and 70 or 80 centims. long), special forms of glass apparatus, etc. *The theory of the operation* is simple: a weighed quantity of a substance is burnt to carbonic acid gas ($CO_2=44$) and water ($H_2O=18$), and these products collected and weighed; 12 parts in every 44 of carbonic acid gas $(=\frac{3}{11})$ are carbon, 2 in every 18 of water $(=\frac{1}{9})$ are hydrogen; nitrogen, if present, escapes as gas. If nitrogen be a constituent, a second quantity is strongly heated with a mixture of the hydrates of sodium and calcium; these bodies then split up into oxides, oxygen, and hydrogen; the oxygen burns the carbon of the substance to carbonic acid gas, its hydrogen and nitrogen appearing as water and ammonia respectively; the carbonic acid and water are disregarded, the ammonia collected and weighed in the form of the double chloride of platinum and ammonium ($PtCl_4,2NH_4Cl = 442{\cdot}8$), of which 28 parts in every 442·8 are nitrogen. The difference between the sum of the weights of hydrogen and carbon, and the weight of substance taken, is the proportion of oxygen in the body, supposing nitrogen to be absent. If nitrogen is present, the difference between the sum of the percentages of carbon, hydrogen, and nitrogen, and 100, is the percentage of oxygen. Shortly, carbon is estimated in the form of carbonic acid gas, hydrogen as water, nitrogen as ammonia, and oxygen by difference.

The following is the outline of the necessary manipulations:—The source of the oxygen for the combustion of carbon and hydrogen is black oxide of copper in coarse powder. 200 or 300 grammes of this material are heated in a crucible to low redness for a short time to expel every trace of moisture—then transferred to store-tubes (fig. 85) resembling test-tubes, half a mètre long, and having a slightly narrowed mouth, the tube being held in a cloth to protect the hand while the hot oxide is being directly introduced into the mouth of the tube by a scooping motion. As soon as the well-corked tube is cool, the oxide is poured, portion by portion, into a similar tube (the combustion-tube), but somewhat longer, drawn out to a quill (bent upwards nearly to a right angle) at one end, and not constricted at the mouth. Two such tubes are readily made by softening in the blowpipe-flame two or three centimètres of the central part of a tube about a mètre long, and drawing the halves of the tube apart as shown in the following engraving (fig. 86). The tubes are separated by melting the glass in the middle of the quilled portion. A few décigrammes of fused chlorate of potassium should first be dropped into the tube. After ten

Fig. 85.

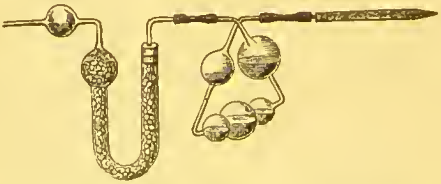
or fifteen centimètres of oxide have been poured in, about a décigramme of the substance to be analysed is dropped down the tube, then a few grammes of oxide, then another décigramme of substance, then more oxide, until three or four décigrammes of the body under examination have been added. The fifteen or twenty centimètres of alternate layers are next thoroughly mixed by a long copper wire having a short helix: more oxide is introduced, the wire cleansed by twisting the helix about in the pure oxide, and a plug of dried asbestos finally placed on the top of the oxide at about five centimètres from the mouth of the tube; the tube is then securely corked and set aside. The substance operated on may be pure white sugar, powdered and dried; the tube in which it is contained is weighed before and after the removal of the portions for combustion; the loss is the quantity employed in the experiment. The combustion-furnace may be such as shown on page 790. If the furnace is very powerful, or the combustion-tube not of the hardest glass, the tube should be enclosed in wire-gauze, the elasticity of which has been destroyed by heating to redness. If the substance under experiment contain nitrogen, the plug of asbestos must be displaced by a roll of copper gauze, which serves to reduce any oxides of nitrogen, and thus ensure the escape of nitrogen itself—or dry yellow chromate of potassium may be used (Perkin). The *water* produced when the prepared tube is heated is collected in a small U-tube containing pieces of chloride of calcium, or pumice-stone moistened with sulphuric acid (fig. 87); the *carbonic acid gas* in a series of bulbs (fig. 87) containing solution of potash (sp. gr. about 1·27). These bulbs may be purchased at any apparatus-shop.

Fig. 86.



The chloride-of-calcium tube is fitted by a good cork to the combustion-tube, the potash-bulbs by a short piece of india-rubber tubing to the chloride-of-calcium tube. The potash-bulbs may carry a short light tube containing a rod of caustic potash three or four centimètres long: this serves to arrest any moisture that might be carried away from the solution of potash by the dried expanded air which escapes during the operation. The combustion-tube having been placed in the furnace, and the drying-tube and potash-bulbs weighed and attached, the gas is lit under the asbestos, and, when the tube is red-hot, the flame slowly extended until nearly the whole tube is at the same temperature, the operation being conducted at such a rate that bubbles of gas escape through the potash-bulbs at about the rate of one per second. When no more gas passes, the extremity of the tube containing the chlorate of potassium is gently heated until oxygen ceases to be evolved; perfect combustion of carbon and removal of all carbonic acid gas is thus ensured. The heating of the chlorate must be very carefully conducted, or the evolution of oxygen may become sufficiently rapid to blow some of the fluid out of the potash-bulbs. The drying-tube and bulbs are disconnected and weighed, the increase in weight due to carbonic acid gas and water respectively noted, and the percentages of carbon, hydrogen, and (by loss) oxygen calculated. This method is that of Liebig, with modifications by Bunsen: good combustion-furnaces are those known as Hofmann's, Griffin's, and others.

Fig. 87.



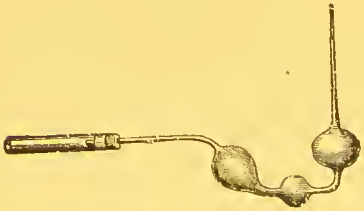
CHLORIDE-OF-CALCIUM TUBE AND POTASH-BULBS.

Chromate of lead can be used for combustions in place of oxide of copper. The advantages are its less hygroscopic nature, and the greater readiness with which it yields its oxygen to organic bodies when heated with them. It must not, however, be used with bodies containing nitrogen, since it would convert so large a proportion of the nitrogen into nitric oxide or higher oxide of nitrogen, that it would be necessary to use an inconveniently long layer of the metallic copper to reduce these oxides and so prevent their absorption in the series of bulbs containing the solution of potash. Organic bodies, however, containing sulphur, bromine, iodine, or chlorine are burnt with advantage by means of chromate of lead. If oxide of copper were used with bodies containing sulphur, it would be necessary to place an additional tube containing peroxide of lead between the chloride-of-calcium tube and the potash-bulbs in order to absorb the sulphurous anhydride formed; this is entirely obviated by using chromate of lead, which itself retains the whole of the sulphur. Again, if bodies containing chlorine, iodine, or bromine are burnt by means of oxide of copper, then volatile chloride, iodide, or bromide of copper is formed, and, collecting in the chloride-of-calcium tube, vitiates the result with regard to the hydrogen; by using chromate of lead, however, the chlorine, iodine, and bromine are respectively retained in the combustion-tube as chloride, bromide, and iodide of lead.

In order to render the chromate fit for use, it is first fused and poured out on a clean iron plate ; when cool, it is powdered and heated in a long tube throughout its whole length, while air, dried by passing through chloride of calcium or strong sulphuric acid, is drawn over it; when the colour of the chromate changes to brown, the heat can be withdrawn and the extremity of the tube farthest from the drying-apparatus closed, so that the air in passing into the tube on cooling may be quite dry; when cool, the drying-tube is removed, and the extremity securely corked ; the chromate of lead is then ready for direct transference to the combustion-tube.

The general manipulations for substances containing nitrogen resemble the foregoing so far as the use of a combustion-tube and furnace and collection of the ammoniacal gas are concerned. The combustion-tube must be quilled at one end, and about a third of a mètre long. The soda-lime is made by slaking quicklime with a solution of soda, of such a strength that about two parts of quicklime shall be mixed with one of hydrate of sodium, drying the product, heating to bright redness, and finely powdering; it should be preserved in a well-closed bottle. Some of the soda-lime is introduced into the tube, then layers of substance and soda-lime, mixture effected by a wire, a good layer of soda-lime added, and a plug of asbestos. Bulbs (fig. 88), known as those of Will and Varrentrapp (the originators of the method), containing hydrochloric acid of about 25 per cent., are then fitted by a cork, and the tube heated in the furnace—to a not too bright red heat, or some of the produced ammonia gas may be decomposed. When gas ceases to pass and combustion is considered to be *quite* complete, the tube is allowed to cool somewhat, the quill is then broken, and aspiration continued slowly until all ammoniacal gas may be considered to have been absorbed by the acid. The bulbs are disconnected, their contents and rinsings poured into a small dish, solution of perchloride of platinum added, and the operation completed as in the estimation of potassium and ammonium salts (*vide* pp. 774 and 777). Or the ammonia may be absorbed by a known quantity of standard sulphuric acid, of which the residual excess is estimated by a standard alkali; certain obvious calculations then giving the amount of ammonia produced.

Fig. 88.



NITROGEN-BULBS.

Conversion into ammonia may also be effected by heating the substance with strong sulphuric acid and, if not then thoroughly attacked, with permanganate of potassium (Kjeldahl). Or the nitrogen may be evolved as gas by heating with oxide of copper and copper-turnings (p. 809) and be collected, over alkali, and its volume, and thus indirectly its weight, be determined.

Liquids are analysed by a similar method to that adopted for solids, volatile liquids being enclosed in small bulbs having a long quill. These are weighed previously to and after the introduction of the liquid; just before being dropped into the combustion-tube the quill is broken *Solids* are also sometimes similarly burnt from a small boat placed in the tube, a continuous current of purified air being used.

Formulæ.—From the percentage composition of an organic substance an empirical formula may be deduced by dividing the weight of each constituent by its atomic weight, and converting the product into the simplest whole numbers; a rational formula by ascertaining the proportion in which the substance unites with a radical or body having a known combining proportion, etc. (*vide* pp. 458–462).

Chlorine, *Bromine*, or *Iodine*, contained in an organic substance may be estimated by heating with fuming nitric acid and nitrate of silver in a sealed tube, or by heating to redness a given weight of the material with ten times as much pure lime in a combustion-tube. Chloride, bromide, or iodide of calcium is thus produced. While still hot, the tube is plunged into water, the mixture of broken glass and powder treated with pure diluted nitric acid in very slight excess; the filtered liquid precipitated by nitrate of silver, and the chloride, bromide, or iodide of silver collected, washed, dried, cooled, and weighed.

Sulphur, *Phosphorus*, and *Arsenium* in organic salts may be estimated by heating with fuming nitric acid in a sealed tube, or by gradually heating in a combustion-tube 1 part of the substance with a mixture of 10 parts nitre, 2 dried carbonate of sodium (in order to moderate deflagration), and 20 chloride of sodium. The product is dissolved in water acidulated by nitric acid, the sulphuric radical precipitated and estimated as sulphate of barium, the phosphoric and arsenic radicals as ammonio-magnesian phosphate or arseniate.

Limit of experimental errors.—Two determinations of carbon may vary to the extent of 0·1 per cent.; of hydrogen, 0·2; of nitrogen, 0·3.

QUININE, ETC.

Process of the British Pharmacopœia for ascertaining the amount of (1) *Quinine with Cinchonidine, and* (2) *Total Alkaloids, in the* Succirubra *or Red Cinchona Bark* (*Cinchonæ Rubræ Cortex*, B.P.).

1. *For Quinine and Cinchonidine.*—Mix 200 grains of red cinchona bark, in No. 60 powder, with 60 grains of hydrate of calcium; slightly moisten the powders with half an ounce of water; mix the whole intimately in a small porcelain dish or mortar; allow the mixture to stand for an hour or two, when it will present the characters of a moist, dark-brown powder, in which there should be no lumps or visible white particles. Transfer this powder to a six-ounce flask, add 3 fluid ounces of a mixture of 3 volumes of commercial benzol and 1 volume of amylic alcohol ("benzolated amylic alcohol," B.P.), boil them together for about half an hour, decant and drain off the liquid on to a filter, leaving the powder in the flask; add more of the benzol liquid to the powder, and boil and decant as before; repeat this operation a third time; then turn the contents of the flask on to the filter, and wash by percolation with more of the liquid until the bark is exhausted. If, during the boiling, a funnel be placed in the mouth of the flask, and another flask filled with cold water be placed in the funnel, this will form a convenient condenser which will prevent the loss of more than a small quantity of the boiling liquid. Introduce the collected filtrate, while still warm, into a stoppered glass separator; add to it 20 minims of diluted hydrochloric acid, mixed with 2 fluid drachms of water; shake them well together, and when the acid liquid has separated this may be drawn off, and the process repeated with distilled water slightly acidulated with hydrochloric acid, until the whole of the alkaloids have been removed. The acid liquid thus obtained will contain the alkaloids as hydrochlorates, with excess of hydrochloric acid. It is to be carefully and exactly neutralized with ammonia, and then concentrated to the bulk of 3 fluid drachms. If now about 15 grains of tartarated soda, dissolved in twice its weight of water, be added to the neutral hydrochlorates, and the mixture stirred with a glass rod, insoluble tartrates of quinine and cinchonidine will separate completely in about an hour; and these col-

lected on a filter, washed, and dried, will contain eight-tenths of their weight of the alkaloids, quinine and cinchonidine, which, divided by 2, represents the percentage of those alkaloids. The other alkaloids will be left in the mother-liquor.

2. *For Total Alkaloids.*—To the mother-liquor from the preceding process add solution of ammonia in slight excess. Collect, wash, and dry the precipitate, which will contain the other alkaloids. The weight of this precipitate divided by 2, and added to the percentage weight of the quinine and cinchonidine, gives the percentage of total alkaloids.

Note.—If it is desired to obtain each alkaloid separately, the above process may be modified by using dilute sulphuric instead of hydrochloric acid for removing the alkaloids from the benzolated amylic alcohol, and exactly neutralizing with ammonia *while kept hot on a water-bath*; on cooling, the quinine will crystallize out almost completely as neutral sulphate. The cinchonidine may then be precipitated from the filtrate by tartarated soda, and, after its removal, quinidine, if present, by iodide of potassium; finally, cinchonine is obtained by precipitating the filtrate from the quinidine with soda or ammonia.

Extractum Cinchonæ Liquidum, B.P.—The greater portion of the alkaloids of red cinchona bark is dissolved out by water acidulated by hydrochloric acid and containing glycerine. The acid, in acting as a solvent, probably more or less decomposes the natural compounds in the bark. The glycerine contributes to the permanence of the preparation. The mixture is evaporated to a low bulk, assayed as follows, and further evaporated or diluted, until 85 fluid parts contain 5 of total alkaloids. 12½ fluid parts of rectified spirit are then mixed in and a little water added to make 100 fluid parts. The *assay* is thus conducted. Place fifty fluid grains of the product of the first evaporation (*a*) with half an ounce of distilled water into a stoppered glass separator capable of holding four fluid ounces; add to this one fluid ounce of benzolated amylic alcohol and half a fluid ounce of solution of soda, shake them together thoroughly and repeatedly, then allow them to remain at rest until the spirituous solution of the alkaloids shall have separated and formed a distinct stratum over the dark-coloured alkaline solution of the other constituents of the extract. Run off the latter by the stopcock, add a little more distilled water to wash away any still adhering alkaline solution from the separator and its contents, and having run off this as before, as completely as possible, decant the spirituous solution into a small porcelain or glass dish the weight of which is known. Evaporate by the heat of a water-bath until a perfectly dry residue is left. The weight now of the dish and its contents, after deducting the known weight of the dish, will give that of the alkaloids, and this multiplied by 2 will give the parts by weight of the alkaloids in 100 fluid parts of the liquid (*a*).

De Vrij's Method for the Separation of the Mixed Alkaloids from Cinchona Barks. De Vrij's Method for the Separation and Quantitative Determination of all the different Cinchona Alkaloids. For these processes the reader is referred to the eleventh edition of this Manual. *Prollius's Method for the Estimation of Total Alkaloids in Cinchona Bark, as modified by De Vrij.—See* the thirteenth edition.

Official (B.P.) *Methods of Testing Sulphate of Quinine for Sulphates of other Alkaloids.*

Test for Cinchonidine and Cinchonine.—Heat 100 grains of the sulphate of quinine in five or six ounces of boiling water, with three or four drops of diluted sulphuric acid. [Paul recommends omission of all acid, except what may be required to ensure perfect neutralization.] Set the solution aside until cold. Separate, by filtration, the purified sulphate of quinine which has crystallized out. [Evaporate to one-fifth.] To the filtrate, which should nearly fill a bottle or flask, add ether, shaking occasionally, until a distinct layer of ether remains undissolved. Add ammonia in very slight excess, and shake thoroughly, so that the quinine at first precipitated shall be redissolved. Set aside for some hours or during a night. Remove the supernatant clear ethereal fluid, which should occupy the neck of the vessel, by a pipette. Wash the residual aqueous fluid and any separated crystals of alkaloid with a very little more ether, once or twice. Collect the separated alkaloid on a tared filter, wash it with a little ether, dry at 212° F. (100° C.), and weigh. Four parts of such alkaloid correspond to five parts of crystallized sulphate of cinchonidine or of sulphate of cinchonine.

Test for Quinidine.—Recrystallize fifty grains of the original sulphate of quinine as described in the previous paragraph. To the filtrate add solution of iodide of potassium, and a little spirit of wine to prevent the precipitation of amorphous hydriodates. Collect any separated hydriodate of quinidine, wash with a little water, dry, and weigh. The weight represents about an equal weight of crystallized sulphate of quinidine.

Test for Cupreine.—Shake the recrystallized sulphate of quinine, obtained in testing the original sulphate of quinine for cinchonidine and cinchonine, with one fluid ounce of ether and a quarter of an ounce of solution of ammonia, and to this ethereal solution, separated, add the ethereal fluid and washings also obtained in testing the original sulphate for the two alkaloids just mentioned. Shake this ethereal liquor with a quarter of a fluid ounce of a ten per cent. solution of caustic soda, adding water if any solid matter separates. Remove the ethereal solution. Wash the aqueous solution with more ether, and remove the ethereal washings. Add diluted sulphuric acid to the aqueous fluid, heated to boiling, until the soda is exactly neutralized. When cold, collect any sulphate of cupreine that has crystallized out on a tared filter; dry, and weigh.

"Sulphate of quinine" should not contain much more than five per cent. of sulphates of other cinchona alkaloids.

Sulphate of quinine normally contains 15·2 per cent. of water; sulphate of cinchonidine 7·0 per cent.; sulphate of cinchonine 6·0 per cent.; all given off at 100° to 115° C. The drying should therefore be effected at 120° C., and the dried salt weighed in well-fitting weighing tubes. 100 parts of cinchonidine are equivalent to 116 parts of anhydrous sulphate of cinchonidine.

Sulphate of cinchonidine is almost the only salt likely to be accidentally present in the sulphate of quinine of trade, much quinidine being rarely present in bark, and sulphate of cinchonine being sufficiently soluble to remain dissolved in the mother-liquors of sulphate of quinine. The sulphate of cinchonidine may vary from 1 to 18 per cent., but more usually is present to the extent of about 6 per cent.

De Vrij's Chromate Test for the purity of sulphate of quinine.—The purity of quinine sulphate may be tested in the following manner (De Vrij):—

Dissolve 1 gramme of the salt in 40 c.c. of hot distilled water and add 6 c.c. of a 5% solution of pure yellow chromate of potassium. Set aside for several hours at a temperature *not above* 15° C., when the quinine will be completely precipitated as chromate. Filter, and after adding a few more drops of the chromate to the filtrate, to make sure that the precipitation has been completed, add 9 or 10 drops of a 5% solution of soda. If the quinine sulphate was pure, the solution will remain clear, even after a day's standing; but if cinchonidine was present, that alkaloid will be precipitated, and may be filtered off and weighed.

Of the Citrate of Iron and Quinine (*Ferri et Quininæ Citras*, B.P.) it is officially stated that "fifty grains dissolved in a fluid ounce of water, and treated with a slight excess of ammonia, give a white precipitate, which, when dissolved by successive treatments of the fluid with ether or chloroform and the latter evaporated and the residue dried (at about 250° F.) until it ceases to lose weight, weighs seven and a half grains. The precipitate is almost entirely soluble in a little pure ether."

A Process for the Determination of the Quinine of the Scaled Compound.—To the residue obtained as stated in the foregoing paragraph is added about 25 c.c. of water and enough diluted sulphuric acid to impart a decidedly acid reaction. The mixture is next heated over a water-bath until, the solution remaining acid, the residue has completely dissolved. Dilute soda solution is afterwards added with great care until the solution is exactly neutral. The dish is then removed and the solution allowed to cool and rest over night, when the quinine will have separated in crystals of ordinary sulphate. These should be collected on a filter, and the mother-liquor tested with litmus-paper. If it is acid, it must be warmed over a water-bath and dilute soda solution added to exact neutralization, and the solution set aside as before, when some more crystals will probably separate. These are also collected and with the former ones washed, dried at 120° C., and weighed [$(C_{20}H_{24}N_2O_2)_2,H_2SO_4=746$]. To this weight must be added 1 gramme for every 750 c.c. of mother-liquor for quinine-sulphate which it retains. From this weight of anhydrous quinine sulphate is calculated its equivalent of hydrous quinine $(C_{20}H_{24}N_2O_2)_2,2H_2O =$ 684, the approximate formula of hydrous quinine dried over a water-bath. The weight thus obtained is compared with the weight of total alkaloid determined, both having been reduced to percentages. The amount of hydrous quinine calculated from the crystals of sulphate should not be much below that weighed directly. In good specimens the difference will be about one per cent.

The sulphate of quinine should yield, according to De Vrij, at least 91·6 per cent. of tartrate of quinine.

(*See* a paper by Fletcher in the *Pharmaceutical Journal* for September 20, 1879; also in that for September 18, 1880, by De Vrij; and in the *Chemist and Druggist* for October, 1885, by Howard.)

MORPHINE.

The official (B.P., 1885) *process for the estimation of this alkaloid in opium* is the Hager-Jacobsen method somewhat modified, and is conducted in the following manner:—

Test.—Take of powdered opium, dried at 212° F. (100° C.), 140 grains; lime, freshly slaked, 60 grains; chloride of ammonium, 40 grains; rectified spirit, ether, distilled water, of each a sufficiency. Triturate together the opium, lime, and 400 grain-measures of distilled water in a mortar until a uniform mixture results; then add 1,000 grain-measures of distilled water and stir occasionally during half an hour. Filter the mixture through a plaited filter about three inches in diameter into a wide-mouthed bottle or stoppered flask (having the capacity of about six fluid ounces and marked at exactly 1,040 grain-measures) until the filtrate reaches this mark. To the filtered liquid (representing 100 grains of opium) add 110 grain-measures of rectified spirit and 500 grain-measures of ethor, and shake the mixturo; then add the chloride of ammonium, shake well and frequently during half an hour, and set it aside for twelve hours. Counterbalance two small filters; place one within the othor in a small funnel, and docant the ethereal layer as completely as practicable upon the inner filter. Add 200 grain-measures of ether to the contents of the bottle, and rotate it; again decant the ethereal layer upon the filter, and afterwards wash the latter with 100 grain-measures of ether added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the bottle in portions, in such a way as to transfer the greater portion of the crystals to the filter. When the fluid has passed through the filter, wash the bottle, and transfer the remaining crystals to the filter, with several small portions of distilled water, using not much more than 200 grain-measures in all, and distributing the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing between sheets of bibulous paper, and afterwards at a temperature between 131° and 140° F. (55° and 60° C.), and finally, at 194° to 212° F. (96° to 100° C.) [110° C. is best]. Weigh the crystals in the inner filter, counterbalancing by the outer filter. The crystals should weigh ten grains, or not less than nine and a half and not more than ten and a half grains, corresponding to about ten per cent. of morphine in the dry powdered opium.

Notes.—The foregoing process, in common with other trustworthy processes of the date (1885), yields results almost exactly comparable amongst themselves; therefore is medically reliable. It has been generally recognised as involving some loss of morphine, the loss being, however, apparently fairly constant. Teschemacher and Smith, after working for many years on the subject, have devised such a combination of known morphiometric methods as enable them to obtain more morphine from a given sample of opium than they formerly obtained, and about 1·7 per cent. more morphine from a given sample than they can obtain by the official method. They hope to so extend their improvements as to obtain still higher results. Meanwhile they claim for their method not only the important medical desideratum that, like other trustworthy methods, it yields constant results, but that it necessarily yields results at all events nearer to truth than the results hitherto obtained. The maximum contents by the official process is to be 10½ per cent. of morphine from the dried opium. This corresponds to a yield by the following process of 12 or 12½ per cent.

Teschemacher and Smith's Method.—Thoroughly exhaust 200 grains of opium with warm distilled water. Concentrate this watery extract to a thin syrup in a shallow dish, over a water bath, the water of which should not quite boil. Transfer this thin syrup to a suitable flask, which permits the use of a soft cork, using a few drops of water successively, to wash out the dish. Add to the contents of the flask 50 fluid grains of alcohol, sp. gr. about 0·820, and about 600 fluid grains of ether. Mix gently, but thoroughly, and then add some 50 fluid grains of ammonia, sp. gr. 0·935. Shake the contents of the flask well to precipitate the alkaloids in arenaceous crystals, with occasional agitation during the ensuing eighteen hours. Transfer the contents of the flask to a vacuum filter, and permit all the adherent liquid to be drawn away, washing out the flask with morphinated spirit,* and continue its use till the liquid passes colourless. Then wash with morphinated water,† till this also passes colourless. Now dry, slowly at first, finishing at 212° F. Transfer the dried substance to a mortar, reduce it to a very fine powder, and digest it thoroughly in benzene to dissolve the narcotine and such of the opium alkaloids, other than morphine, which may be present. Transfer this mixture to a vacuum filter, wash out the mortar carefully with benzene, which use to wash the powder thoroughly. This, then, will be morphine, free from other opium alkaloids and narcotine, but still containing colouring and possibly other organic matters to the extent of 3 to 10 per cent. Dry and weigh this powder. Now ascertain the percentage by weight of crystallized morphine by titration of this powder with standard hydrochloric acid and litmus as the indicator. (This acid is so made that 1,000 grains by weight shall exactly neutralize 100 grains of pure morphine crystallized from water, washed with ether, and gently dried finally at 212° F.)

Of Hydrochlorate of Morphine it is officially stated that "twenty grains of the salt, dissolved in half an ounce of warm water, with ammonia added in the slightest possible excess, give on cooling a crystalline precipitate which, when washed with a little cold water and dried in a water-bath, weighs 16 grains": and, respecting the *Injectio Morphinæ Hypodermica*, B.P., "a fluid drachm of it rendered slightly alkaline by the addition of solution of ammonia yields a precipitate of morphine which, after being washed and dried, should weigh 4·25 grains, corresponding to six grains of acetate of morphine. The acetate (*Morphinæ Acetas*, B.P.) is liable to lose acetic acid and become basic, hence the following official requirements: "Twenty grains of the salt form with one drachm of water a slightly turbid solution, which is rendered clear by the addition of one grain of acetic acid; and this solution, when mixed with ammonia in slight excess, yields a precipitate which, after washing with a little cold water and drying in a water-bath, weighs fifteen grains. If the salt yields a larger proportion of morphine than this, it should be recrystallized from hot water acidulated with acetic acid."

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* *Morphinated Spirit.*—Digest a large excess of morphine in rectified spirit of 80 per cent., for several days, with frequent agitation. Filter for use.

† *Morphinated Water.*—As above, substituting distilled water for spirit.

NUX-VOMICA ALKALOIDS.

The British Pharmacopœia directs that its two galenical preparations of nux vomica (*Extractum Nucis Vomicæ* and *Tinctura Nucis Vomicæ*) shall contain defined proportions of the mixed alkaloids of the drug.——The *Extract* is made by exhausting a pound of powdered nux vomica with a mixture of 64 fluid ounces of rectified spirit and 16 of water by percolation. One ounce of the percolate is treated as follows:—Evaporate almost to dryness over a water-bath, to dispel spirit; dissolve the residue in half a fluid ounce of diluted sulphuric acid, with an equal bulk of water and add two fluid drachms of chloroform; agitate and warm gently. When the liquors have separated, draw off and reject the chloroform; then add to the acid liquor excess of solution of ammonia and half a fluid ounce of chloroform; well agitate, gently warm, and, after the liquors have completely separated, transfer the chloroform to a weighed dish, evaporate over a water-bath, and dry for one hour at 212° F. (100° C.). Allow the residue of total alkaloid to cool, and then weigh it. Take of the percolated liquid as much as shall contain 131¼ grains of total alkaloid, distil off the spirit, and evaporate over a water-bath until the Extract weighs two ounces. This Extract will contain 15 per cent. of total alkaloid.——The *Tincture* is prepared by dissolving 133 grains of the assayed Extract in a pint of diluted spirit (made by adding enough rectified spirit to four ounces of water to produce a pint of fluid). One fluid ounce of this Tincture will contain one grain of the alkaloids of nux vomica.——If properly prepared, ten grains of the *Extract* when treated in the following manner should yield one and a half grains of total alkaloid. Dissolve the Extract in half a fluid ounce of water, with the aid of a gentle heat, and add a drachm of carbonate of sodium previously dissolved in half a fluid ounce of water, and half a fluid ounce of chloroform; agitate, warm gently, and separate the chloroform. To the separated chloroform add half a fluid ounce of diluted sulphuric acid with an equal bulk of water; again agitate, warm and separate the acid liquid from the chloroform. To this acid liquor add now an excess of ammonia, and agitate with half a fluid ounce of chloroform; when the liquors have separated, transfer the chloroform to a weighed dish, and evaporate the chloroform over a water-bath. Dry the residue for one hour, and weigh.

SUGAR.

The qualitative test for sugar, by means of an alkaline copper solution (*vide* p. 557), may be applied in the estimation of sugar in sacchariferous substances.

Process 1.—34·65 grammes of pure dry crystals of ordinary sulphate of copper are dissolved in about 250 c.c. of distilled water. 173 grammes of pure crystals of the double tartrate of potassium and sodium are dissolved in 480 c.c. of solution of caustic soda of sp. gr. 1·14. The solutions are *only mixed when required*, water being then added to form 1 litre; smaller quantities of the fluids being proportionately diluted. 100 c.c. of this mixture represent 3·465 grammes of sulphate of copper, and correspond to 0·500 of a gramme of pure anhydrous grape-sugar, 0·475 of cane-sugar, 0·807 of maltose, or

0·450 of starch. The solutions must be preserved in well-stoppered bottles to prevent absorption of carbonic acid, and be kept in a dark place. Should the mixture give a precipitate on boiling, a little solution of soda may be added when making experiments. Such a reagent is known as *Fehling's solution.*

Dissolve 0·475 of pure dry powdered cane-sugar in about 50 c.c. of water, convert into grape-sugar by acidulating with sulphuric acid and heating for an hour or two on a water-bath, make slightly alkaline with carbonate of sodium, and dilute to 100 c.c. Place 10 c.c. of the copper solution in a small flask, dilute with three or four times its bulk of water, and gently boil. Into the boiling liquid drop the solution of sugar from a burette, one cubic centimètre, or less, at a time, until, after standing for the precipitate to subside, the supernatant liquid has just lost its blue colour; 10 c.c. of the solution of sugar should be required to produce this effect—equivalent to 0·0475 of cane sugar, 0·0807 of maltose, or 0·0500 of grape-sugar. Experiments on pure cane-sugar must be practised until accuracy is attained; syrups, diabetic urine, and saccharated substances containing unknown quantities of sugar may then be analysed.

Starch is converted into grape-sugar by gentle ebullition with diluted acid for eight or ten hours, the solution being finally diluted so that one part of starch, or rather sugar, shall be contained in about 150 of water.

If, instead of Fehling's solution, Pavy's ammoniated solution be used (*Proceedings of the Royal Society*, vol. xxviii. p. 260; and vol. xxix. p. 272; or *Lancet*, March 1, 1884, p. 376; or *Pharmaceutical Journal*, 3 ser., vol. xvii. p. 856), one-fifth more of the copper salt will be required to do the same amount of work.

In cases in which loss of blue colour cannot be relied on as indicating the termination of the reaction, the suboxide of copper should be rapidly filtered out, washed, dried, and, after adding the filter-ash, ignited, and the resulting black oxide of copper weighed. One gramme of black oxide (or of suboxide or of metallic copper) indicates the subjoined amounts of the respective sugars.

One gramme of	Glucose.		Cane sugar.		Milk sugar.		Malt sugar.
Black oxide	·4535	—	·4308	—	·6153	—	·7314
Suboxide	·5042	—	·4790	—	·6843	—	·8132
Metallic copper . .	·5634	—	·5395	—	·7707	—	·9089

Process 2.—Roberts's Method for the Estimation of Sugar in Urine.—About four ounces of saccharine urine are put into a twelve-ounce bottle, and a lump of German yeast about the size of a cob-nut or small walnut is added. This excess of yeast hastens fermentation, and does no harm. The bottle is then covered with a grooved cork (to allow of the escape of carbonic acid gas), and set aside in a warm place to ferment. By the side of it is placed a tightly-corked four-ounce phial filled with the same urine without any yeast. In about twenty-four hours the fermentation will have ceased and the scum cleared off or subsided. The fermented urine is then decanted, and its specific gravity taken. At the same time the specific gravity of the unfermented urine in the companion phial is observed. The *density lost* is thus ascertained. Each degree of density lost represents a grain of glucose per fluid ounce.

Sugar is often estimated by the measurement of the carbonic acid gas evolved, or of the alcohol produced, during fermentation.

Saccharometry.—A generic term for certain quantitative operations undertaken with the view of ascertaining the quantity of sugar present in any matter in which it may be contained.

Saccharometry is frequently performed upon common syrup (*Syrupus*, B.P.) and solutions which are known to contain nothing but cane- (ordinary) sugar, the object being merely to ascertain the amount present. In such a case it is only necessary to take the specific gravity of the liquid at 60° F., and then refer to a previously prepared Table of densities and percentages.

Specific gravity.	Sugar, per cent.	Specific gravity.	Sugar, per cent.	Specific gravity.	Sugar, per cent.
1·007	1·8	1·100	23·7	1·210	46·2
1·014	3·5	1·108	25·6	1·221	48·1
1·022	5·2	1·116	27·6	1·231	50·0
1·029	7·0	1·125	29·4	1·242	52·1
1·036	8·7	1·134	31·5	1·252	54·1
1·044	10·4	1·143	33·4	1·261	56·0
1·052	12·4	1·152	35·2	1·275	58·0
1·060	14·4	1·161	37·0	1·286	60·1
1·067	16·3	1·171	38·8	1·298	62·2
1·075	18·2	1·180	40·6	1·309	64·4
1·083	20·8	1·190	42·4	1·321	66·6 ?
1·091	21·8	1·199	44·3	1·330 (B.P.)	66·6 ?

The spec. grav. may be taken by a hydrometer, technically termed a *saccharometer*. (The above spec. gravs. = 1° to 35° Baumé.)

If a liquid contains other substances besides cane-sugar, the test of specific gravity is of little or no value. Advantage may then be taken of the fact that syrup causes right-handed twisting of a ray of plane-polarized light to an extent proportionate to the amount of sugar in solution. The saccharine fluid is placed in a long tube having opaque sides and transparent ends; and a ray of homogeneous light, polarized by reflection from a black-glass mirror or otherwise, is sent through the liquid and optically examined by a plate of tourmaline, Nicol's prism, or other polarizing eyepiece. Attached to the eyepiece is a short arm which traverses a circle divided into degrees. The eyepiece and arm are previously so adjusted that when the ray is no longer visible the arm points to the zero of the scale of degrees. The saccharine solution, however, so twists the ray as to again render it visible; and the number of degrees which the eyepiece has to be rotated before the ray is once more invisible is proportionate to the strength of the solution. The value of the degrees having been ascertained by direct experiment, and the results tabulated, a reference to the table indicates the percentage of sugar in the liquid under examination. Grape-sugar also possesses the property of dextral rotation, but less powerfully than cane-sugar; moreover, the former variety does not, like cane-sugar, suffer inversion of the direction of rotation on the addition of hydrochloric acid to its solution—an operation that furnishes data for ascertaining the amount of cane- and of grape-sugar, or of crystallizable and non-crystallizable sugar, present in a mixture. In using the polariscope saccharometer, it is convenient to employ tubes of uniform size, and always to operate at the same temperature. Various modes are adopted of applying for quantitative purposes this action of syrup on polarized light.

ALCOHOL.

Mulder's process for the determination of the amount of alcohol in wine, beers, tinctures, and other alcoholic liquids containing vegetable matter is as follows :—Take the specific gravity and temperature of the liquid, and measure off a certain quantity (100 cubic centimètres); evaporate to one-half or less, avoiding ebullition in order that particles of the material may not be carried away by the steam. Dilute with water to the original bulk, and take the specific gravity at the same temperature as before. Of the figures representing the latter specific gravity, all over 1,000 show to what extent dissolved solid matter affected the original specific gravity of the liquid. Thus, the specific gravity of a sample of wine at 15·5° C. is 0·9951; evaporated till all alcohol is removed and diluted with water to the original bulk, the specific gravity at 15·5° C. is 1·0081 : 0·0081 represents the gravitating effect of dissolved solid matter in 0·9951 part of original wine. 0·0081 subtracted from 0·9951 leaves 0·987, which is the specific gravity of the alcohol and water of the wine. Or, divide the sp. gr. of the wine by the sp. gr. of the wine minus alcohol, carrying out the sum to four places of decimals; the quotient shows the sp. gr. of the water and alcohol only of the wine. On referring to a table of the strengths of diluted alcohol of different specific gravities, 0·987 at 15·5° C. is found to indicate a spirit containing 8 per cent. of real alcohol. If the foregoing operation be conducted in a retort, the liquid being boiled and the steam carefully condensed, the distillate, diluted with water to the original bulk of wine operated on, will still more accurately represent the amount of water and alcohol in the wine—its specific gravity showing the percentage of real alcohol present.

DIALYSIS.

Dialysis (from διὰ, *dia*, through, and λύσις, *lusis*, a loosing or resolving) is a term applied by Graham to a process of analysis by diffusion through a septum. The apparatus used in the process is called a *dialyzer*, and is constructed and employed in the following manner. The most convenient septum is the commercial article known as *parchment paper*, made by immersing unsized paper for a short time in sulphuric acid; it is sold by most dealers in chemical apparatus. A piece of this material is stretched over a gutta-percha hoop, and secured by a second external hoop. Dialyzers of useful size are one or two inches deep and five to ten inches wide. Liquids to be dialyzed are poured into the dialyzer, which is then floated in a flat dish containing distilled water. The portion passing through the septum is termed the *diffusate*, the portion which does not pass through is termed the *dialysate*.

The practical value of dialysis depends upon the fact that certain substances will diffuse through a given septum far more rapidly than others. Uncrystallizable bodies diffuse very slowly. Of such matters as starch, gum, albumen, and gelatine, the last-named is perhaps least diffusive; hence substances of this class are termed *colloids*, or bodies like *collin*, which is the soluble form of gelatine. Substances which diffuse rapidly are mostly crystalline; hence bodies of this class are termed *crystalloids*.

Solution of dialysed iron, *Liquor Ferri Dialysatus*, B.P., an aqueous solution of about 5 per cent. of highly basic oxychloride of iron is obtained by saturating one fluid ounce of the solution of perchloride of iron with fresh ferric hydrate (obtained by precipitating six fluid ounces of the same solution by ammonia, and washing and draining the product), filtering if necessary, placing on a dialyser floating in distilled water, and displacing the fluid in the dish by water daily for a week or two, or until the diffusate gives no reaction with nitrate of silver, and the fluid on the dialyser is almost tasteless. The colloid fluid which has thus been subjected to dialysis (hence the only title to the name *dialysed iron*), and which does not pass through the dialyser, is the highly basic oxychloride of iron, or so-called "dialysed iron," or "dialytic iron." This fluid has very little taste of iron. Its value as a medicine has been questioned, its non-diffusibility suggesting that it never passes out of the intestinal canal, and therefore never gets into the blood. Possibly it becomes decomposed in the system and the resulting product becomes assimilated.

It is "a clear dark reddish-brown liquid, free from any marked ferruginous taste." Neutral to test-papers. Specific gravity about 1·047. The solution gives no precipitate with ferrocyanide of potassium or with nitrate of silver, but after being heated with hydrochloric acid it yields with ferrocyanide of potassium a blue precipitate. 100 grains by weight afford a precipitate with solution of ammonia, which, washed, dried, and ignited, weighs 5 grains.

The phenomena of dialysis show that crystalloids are superior to colloids in affinity for water.

QUESTIONS AND EXERCISES.

Carbonate of potassium is said to lose 16 per cent. of water on exposure to a red heat; give the details of manipulation observed in verifying this statement.—Write a few paragraphs descriptive of the process of ultimate organic analysis.—In what forms are carbon, hydrogen, and nitrogen weighed in quantitative analysis?—In the combustion of ·41 of a gramme of sugar, what weights of products will be obtained? *Ans.*, ·632 of carbonic acid gas (CO_2) and ·237 of water (H_2O).—How is cinchona assayed for mixed alkaloids?—Give the official method for the estimation of morphine in opium.—Mention the operations necessary for the estimation of the proportion of sugar in saccharated carbonate of iron, or in a specimen of diabetic urine.—What is understood by *saccharometry?*—Give two processes for the estimation of the percentage of alcohol in tinctures, wines, or beer.—Define dialysis.

CONCLUSION.

Detailed instructions for the quantitative analysis of potable water, articles of food, general technical products, special minerals, soils, manures, air, illuminating agents (including solid fats, oils, spirits, petroleum, and gas), dyes, and tanning-materials, would scarcely be in place in this volume.

The course through which the reader has been conducted will, it is hoped, have taught him the principles of the science of chemistry, and given him special knowledge concerning the applications of that science to medicine and pharmacy, as well as have imparted sufficient manipulative skill to meet the requirements of manufacture or analysis. The author would venture to suggest that this knowledge be utilized, not only in the way of personal advantage, but in experimental researches on chemical subjects connected with pharmacognosy, pharmacology, therapeutics and pharmacy. The discovery and publication of a new truth, great or small, is the best means whereby to aid in advancing the calling in which we may be engaged, increase our own reputation, and contribute to that "ultimate end of knowledge" which Bacon described as "employing the Divine gift of reason to the use and benefit of mankind."

INSTRUCTIONS TO BINDER.

“Starches” should face page 566.

“Urinary Deposits,” 1, } { should face each other be-
“Urinary Deposits,” 2, } { tween pages 696 and 697.

APPENDIX.

TABLE OF OFFICIAL TESTS FOR IMPURITIES IN PREPARATIONS OF THE BRITISH PHARMACOPŒIA.*

Name of Preparation.	Impurities.	Test.	Page.
Acaciæ Gummi	Starch	Iodine	564
Acetanilidum	Mineral matter	Incineration	110
	Other organic matter	Sulphuric acid	Chars
	Acetone, etc.	Ferric chloride	Colour
Acetum	More than one-thousandth of Sulphuric Acid.	Quantitative analysis	800
Acidum Aceticum	Traces of Lead or Copper	Sulphuretted Hydrogen	298
	Sulphuric acid	Soluble barium salt	364
	Hydrochloric acid	Nitrate of Silver, etc.	311
	Sulphurous acid	Nascent Hydrogen	359
	Mineral matter	Evaporation and ignition	110
Acid. Acetic Glaciale	Sulphurous acid	Nascent Hydrogen	359
Acidum Boricum	Alkaline salts	Insolubility in Alcohol	394
	Sulphates	Soluble barium salt	364
	Chlorides	Nitrate of Silver	311
	Calcium salts	Oxalate of Ammonium	128
	Iron salts, etc.	Sulphydrate of Ammonium	181
	Sodium salts	Flame test	95
Acidum Chromicum	Excess of Sulphates	Ppt. with barium salt, etc.	364
Acidum Citricum	Traces of Copper or Lead	Sulphuretted Hydrogen	298
	Tartaric acid	Acetate of Potassium	379
	Tartaric acid	Excess of Lime-water	384
	Sulphuric acid	Soluble barium salt, etc.	364
	Mineral matter	Incineration	110
Acidum Gallicum	Tannic acid	(Isinglass) Gelatine	423
Acidum Hydrobromicum Dilutum	Fixed matter	Evaporation	110
	Sulphates	Soluble barium salt, etc.	364
	Traces of some acids	Colour on keeping	
	General	Quantitative analysis	752
Acidum Hydrochloricum	Sulphuric acid	Soluble barium salt	364
	Arsenium	Sulphuretted Hydrogen	298
		Copper	194
	Sulphurous acid	Nascent Hydrogen	359
	Chlorine	Sulphate of Indigo	339
Acidum Hydrocyanicum Dilutum	Sulphuric acid	Soluble barium salt	364
	Hydrochloric acid	Nitrate of Silver, etc.	311
Acidum Lacticum	Iron, Lead, etc.	Ammonia and Sulphydrate	257
	Sulphates	Soluble barium salt	364
	Chlorides	Nitrate of Silver, etc.	311
	Calcium Salts	Oxalate of Ammonium	128
	Sugar	Alkaline copper solution	557
	General	Quantitative analysis	752
Acidum Meconicum	Alkaloids	Iodine and Iod. Potassium	682

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* The manipulations necessary to be observed in testing for impurities will be found described in the paragraphs treating of those substances. The Table also includes references to processes for ascertaining deficiency in strength of official articles.

The other "characters and tests" of pharmacopœial chemical compounds have been given in connection with the respective synthetical and analytical reactions.

Name of Preparation.	Impurities.	Test.	Page.
Acidum Nitricum	Mineral matter	Evaporation and ignition	110
	Sulphuric acid	Soluble barium salt	364
	Hydrochloric acid	Nitrate of Silver, etc.	311
Acidum Oleicum	Stearic and Palmitic acids	Lead salt insoluble in ether	547
Acidum Oxalicum	Mineral matter	Incineration	110
Acidum Phosphoricum Concentratum *vel* Dilutum	Arsenium, Lead, Platinum	Sulphuretted Hydrogen	298
	Sulphuric acid	Soluble barium salt	364
	Hydrochloric acid	Nitrate of Silver, etc.	311
	Metaphosphoric acid	Albumen	413
	Nitric acid	Ferrous sulphate, etc.	337
	Phosphorous acid	Corrosive sublimate	417
	Ammonium (phosphate)	Hot alkali	106
	Calcium salts	Oxalate of Ammonium, etc.	128
	Excess of Water	Quantitative analysis	804
Acidum Salicylicum	Iron; organic impurities	Colour on evaporation	588
Acidum Sulphuricum	Mineral matter	Evaporation and ignition	363
	Excess of Water	Quantitative analysis	753
	Arsenium	Stannous Chloride	198
Acidum Sulphurosum	Sulphuric acid	Soluble barium salt	364
Acidum Tannicum	Mineral matter	Incineration	110
Acidum Tartaricum	Metallic matter, as Lead	Sulphuretted Hydrogen	298
	Oxalic acid	Sulphate of Calcium	372
	Calcium salts	Oxalate of Ammonium	128
	Mineral matter	Incineration	110
Aconitina	Mineral matter	Incineration	110
Adeps Lanæ	Other fats	Melting-point, etc.	548
	Mineral matter	Incineration	110
	Excess of fatty acid	Soda	548
	Nitrogenous matter	Hot soda	548
Adeps Lanæ Hydrosus	Excess of water	Evaporation	548
Adeps Præparatus	Chloride (of Sodium)	Nitrate of silver, etc.	311
	Starch (flour)	Iodine	564
	Lime	Incineration, etc., as for gum	126
Æther	Alcohol	Boiling-point, sp. gravity	527
Æther Aceticus	Water, Alcohol	Spec. grav. and boiling-point	484
Æther Purus	Alcohol, Water	Specific gravity	527
	Undetermined org. matter	Iodide of Potassium	527
Alcohol Ethylicum	Resin or oil	Opalescence on dilution	529
	Water	Anhyd. cop. sulph., sp. gr.	529
	Fixed matter	Incomplete volatility	529
Alcohol Amylicum	Other spirituous matter	Boiling-point, sp. gravity	535
Alum	Iron (sulphate)	Yellow or red Prussiate	181
Ammonii Benzoas	Fixed salts	Non-volatility	107
Ammonii Bromidum	Bromates	Diluted Sulphuric Acid	315
	Iodides	Starch mucilage	318
	Sulphates	Soluble barium salt, etc.	364
	General	Volumetric analysis	757
Ammonii Carbonas	Fixed salts	Non-volatility	107
	Sulphates	Soluble barium salt, etc.	364
	Chlorides	Nitrate of Silver, etc.	311
Ammonii Chloridum	Fixed salts	Non-volatility	107
Ammonii Nitras	Chlorides	Nitrate of Silver, etc.	311
	Sulphates	Soluble barium salt, etc.	364
Amylum	Alkaline matter	Red Litmus	103
	Acid matter	Blue Litmus	103
Amyl Nitris	General	Fractional distillation	486
Antimonium Nigrum Purificat.	Silica	Insol. in Hydrochloric acid	419
	Soluble Arsenium salt	The copper test	194
Antimonii Oxidum	Higher oxides of Antimony	Insolubility in sol. of acid tartrate of potassium	206
Antimonium Sulph.	General	Quantitative analysis	786

Name of Preparation.	Impurities.	Test.	Page.
Antimonium Tart.	General	Quantitative analysis	786
Aqua Aurantii Floris	Metallic (Pb, Cu, Sn)	Sulphuretted Hydrogen	298
Aqua Destillata	Fixed salts	Evaporation and ignition	110
	Tin, Lead, or Copper	Sulphuretted Hydrogen	298
	Calcium salts	Oxalate of Ammonium	128
	Chlorides	Nitrate of Silver, etc.	311
	Sulphates	Soluble barium salt, etc.	364
	Excess of Ammonia	Nessler's reagent	745
	Carbonates	Lime-water	369
Argenti Nitras, Argent. et Pot. Nit.	Other nitrates, etc.	Quantitative analysis, etc.	793
Argenti Oxidum	Metallic silver	Effervescence with nitric acid	250
	General	Quantitative analysis	792
Argentum Purificatum	Copper	Ammonia to nitric solution	219
	General	Quantitative analysis	793
Asafœtida	Earthy matter	Incineration	110
Atropina	Mineral matter	Incineration	110
Atropinæ Sulphas	Mineral matter	Incineration	110
Balsamum Peruvianum	Fixed oil	Immiscibility with alcohol	
	Alcohol	Non-diminution of volume when mixed with water	
	Resins, oils, etc.	Slaked lime	590
Beberinæ Sulphas	Mineral matter	Incineration	110
Bismuthi Carbonas	Nitrates	Sulphate of Indigo	339
	Lead (carbonate)	Diluted sulphuric acid	254
	Chlorides	Nitrate of Silver, etc.	311
	Other impurities	*See* Bism. Purif.	
Bismuthi Citras	Phosphate of Calcium	Citric acid, etc.	295
	Nitrates	Ferrous sulphate, etc.	337
	General	Quantitative analysis	788
	Other impurities	*See* Bism. Purif.	
Bismuthi et Ammonii Citras	General	Quantitative analysis	788
	Other impurities	*See* Bism. Purif.	
Bismuthi Oxidum	Moisture Carbonate (of Bismuth)	Heated it loses weight	806
	Lead compounds	Sulphuric acid	246
	Chlorides	Nitrate of Silver, etc.	311
	Silver	HCl after sep. of Bi by AmHO	251
	Phosphate of Calcium	Citric acid, etc.	295
	Other impurities	*See* Bism. Purif.	
Bismuthi Subnitras	Lead (oxynitrate)	Diluted sulphuric acid	246
	Chlorides	Nitrate of Silver, etc.	311
	Silver	Hydrochloric acid	251
	Phosphate of Calcium	Citric acid, etc.	295
	Other impurities	*See* Bism. Purif.	
Bismuthum Purificatum	Arsenium	Marsh's test	194
	Silver	Hydrochloric acid	251
	Lead	Diluted sulphuric acid	246
	Tellurium and Selenium	Sulphurous acid	295
	Copper	Ammonia	219
	Iron	Ferrocyanide of Potassium	295
Borax	General	Quantitative analysis	746
Bromum	General	Sp. gr. (726) ; boiling-point	713
	Iodine	Starch	317
Calcii Carbonas Præcipitata	Alumina, Magnesia, Ferric Oxide, Phosphates.	Sacc. solution of Lime, etc.	117
	Chlorides	Nitrate of Silver, etc.	311
Calcii Chloridum	Hypochlorite of Calcium	Hydrochloric acid	345
	Carbonic acid	Lime-water	370
Calcii Hypophosphis	Soluble Phosphate	Acetate of Lead	408
	General	Permanganate of Potassium	408

Name of Preparation.	Impurities.	Test.	Page.
Calcii Phosphas	Carbonates (of Calcium)	Effervescence with acids	370
	Alumina	Solution of Potash, etc.	156
	Sand	Insolubility in acid	420
	More than traces of chlorides	Nitrate of Silver, etc.	311
	General	Quantitative analysis	803
Calx	Carbonate of Calcium	Effervescence with acids	370
	Alumina, Oxide of Iron, etc.	Sacc. sol. of Lime, etc.	117
Calx Chlorinata	General	Quantitative analysis	770
Calx Sulphurata	General	Quantitative analysis	126
Cambogia	Starch	Iodine (Green)	564
	Rice, flour, sand, powdered bark	Microscope, after exhausting with spt. and with cold water	
Camphora	Fixed salts	Non-volatility	502
Carbo Animalis Pur.	Earthy salts	Incineration	110
Carbo Ligni	More than 2 per cent. of ash	Incineration	110
Catechu	Starch	Iodine	564
Cera Alba Cera Flava	Soft fats, paraffin, etc.	Melting-point	714
	Resin	Solubility in alcohol, etc.	536
	Insoluble portion of comb	Insolubility in turpentine	
	Flour	Iodine	564
	Fat acids, Japan wax	Soda, acid, etc.	536
	Soap	Water and acid, etc.	536
Cerii Oxalas	Carbonates and other oxalates	Ash sol. in acids with effervescence	263
	Alumina	Insol. hydrate in ammonia	263
	General	More or less than 48 per cent. of ash	263
Cetaceum	Soft Fats	Melting-point	714
Chloral Hydras	Free acid	Litmus-paper	578
	Other organic bodies	Sulphuric acid	581
	General	Quantitative analysis	581
Chloroform	General	Specific gravity	478
	Hydrocarbons	Sulphuric acid	478
	Non-volatile matter	Residue on evaporation	478
	Alcohol (? impurity)	Lieben's test	478
Cinchonidinæ Sulphas	Cinchonine	Ammonia after tartrate, etc.	627
	Foreign organic matter	Chars with sulphuric acid	627
	Mineral matter	Incineration	110
Cinchoninæ Sulphas	Foreign organic matter	Chars with sulphuric acid	627
	Mineral matter	Incineration	110
Coccus	Mineral matter	More than 1 per cent. of ash	110
Colocynthidis Pulpa (in powder)	Starch	Iodine	564
	Powder of the seeds	Ether extracts oil	546
Copaiba	Fixed oils	Soft residue on evaporation	508
	Turpentine	Odour during evaporation	508
	Wood oil	Soluble in absolute alcohol	507
		Soluble in petroleum spirit	507
Creasotum	Carbolic acid	Oxidation	540
		Non-volatility at 212° F.	540
		Dextro-rotation of polar. ray	540
		Crystallization on cooling	540
Creta Præparata	Alumina, Magnesia, Ferric Oxide, Phosphates	Saccharated sol. of lime, etc.	117
Crocus	Earthy matter	Sediment in infusion, etc.	660
Cupri Sulphas	More than traces of Iron	Chlorine and ammonia	181
Elaterium	Carbonates (chalk)	Effervescence with acids	370
	General	Quantitative analysis	600
Fel Bovinum Purificatum	Mucus, crude bile	Incomplete solubility in spirit	649
Ferri Arsenias	Sulphates	Soluble barium salt, etc.	364
	General	Quantitative analysis	766

Name of Preparation.	Impurities.	Test.	Page.
Ferri Carbonas Saccharata	Sulphates	Soluble barium salt, etc.	364
	General	Quantitative analysis	766
Ferri et Ammonii Citras	Tartrate (of Iron and Ammonium)	Ebullition with potash and saturation with acetic acid	384
	General	Quantitative analysis	784
	Potassium or Sodium (salts)	Alkalinity of ash	103
Ferri et Quininæ Citras	Potassium or Sodium (salts)	Alkalinity of ash	103
	General	Quantitative analysis	818
	Alkaloids other than quinine	Pptd. alkaloid insol. in ether	818
Ferri Peroxidum Hydratum	Ferrous hydrate	Red prussiate to acid solution	180
	Ferric oxide	Absence of moisture	806
Ferri Phosphas	Arsenium (ferri arsenias)	Slip of copper in acid sol.	194
	General	Quantitative analysis	766
Ferri Sulphas Ferri Sulphas Granulata et Exsiccata	Ferric oxysulphate	Insolubility in water	161
	Ferric compounds	Ppt. of sulphur in aq. sol. by sulphuretted hydrogen	180
	Copper, etc.	Sulphuretted hydrogen	298
	General	Quantitative analysis	766
Ferrum Redactum	Less than 50 per cent.	Quantitative analysis	784
	Sulphides	Smell of H_2S with HCl	356
Ferrum Tartaratum	Ferrous compounds	Red prussiate to acid solution	180
	General	Quantitative analysis	784
Glusidum	Other organic matter	Sulphuric acid	Chars
Glycerinum	General	Specific gravity	725
	Chlorides	Nitrate of Silver, etc.	311
	Metals	Sulphydrate of Ammonium	181
	Calcium	Oxalate of Ammonium	128
	Sulphates	Soluble barium salt, etc.	364
	Acid or alkali	Litmus	103
	Other organic matter	Sulphuric acid	544
	Formic or butyric acid	Odour with dil. sulph. acid	
Gossypium	Fatty matter	Not readily wetted	
	Acid or alkali	Litmus	103
	Mineral matter	More than 1 per cent. of ash	110
Homatropinæ hydrobromas	Mineral matter	Incineration	110
	Atropine	Ammonia	635
Hydrarg. Iod. Rub.	Fixed salts	Non-volatility	239
Hydrarg. Ox. Flav.	Fixed salts, as NaCl	Non-volatility	239
Hydrargyri Oxidum Rubrum	Fixed salts	Non-volatility	239
	Nitrates (of Mercury)	Orange vapour on heating	232
Hydrargyri Perchloridum	Calomel	Insoluble in ether	234
	Fixed salts	Non-volatility	239
Hydrargyri Subchloridum	Corrosive Sublimate	Treatment with ether	234
	Fixed salts	Non-volatility	239
Hydrargyri Sulphas	Fixed salts	Non-volatility	239
Hydrargyrum	Fixed metals	Non-volatility	239
Hydrargyrum Ammoniatum	Fixed salts	Non-volatility	239
	Excess Chlor. Ammon.	Fusibility	236
	General	Quantitative analysis	789
Hydrargyrum cum Creta.	Mercuric Oxide	Stannous chloride to solution in hydrochloric acid	238
Injectio Morphinæ Hypodermica	Particles of solid matter	Appearance	822
	General	Quantitative analysis	822
Iodum	Fixed salts	Non-volatility	317
	Cyanide of Iodine	Physical characters	317
	General	Quantitative analysis	769
Jalapa	Tampico Jalap	Solubility of resin	602
Jalapæ Resina	Resin	Solubility in turpentine	602
	Tampico resin	Solubility in ether	602
Limonis Succus	Deficiency of Citric Acid	Quantitative analysis	382
Liquor Ammoniæ	General	Specific gravity	727
		Quantitative analysis	744

Name of Preparation.	Impurities.	Test.	Page.
Liquor Ammoniæ Fortior...	General impurity or deficiency	Specific gravity (726) and Quantitative analysis	744
	Carbonates	Lime-water...	370
	Calcium (Chloride, etc.) ...	Oxalate of Ammonium	128
	Ferrous Hydrate, etc. ...	Sulphydrate of Ammonium ...	181
	Sulphur salts (AmHS) ...	Ammonio-sulphate Copper ...	357
	Chlorides	Nitrate of Silver, etc.	311
	Sulphates	Soluble barium salt, etc. ...	364
Liq. Antim. Chlor.	... ...	... ...	727
Liq. Arsenicalis ...	... ...	... ...	786
Liq. Arsenici Hydrochloricus ...	General impurity or deficiency...	Specific gravity	763
		Quantitative analysis ...	726
Liq. Bismuthi et Ammonii Citratis	... ...	... ...	788
Liq. Calcis	Deficiency in strength ...	Quantitative analysis	747
Liq. Calcis Chlorinatæ	General impurity or deficiency...	Specific gravity	770
Liq. Calcis Saccharatus		Quantitative analysis	747
Liquor Chlori ...	General quality	Specific gravity	727
	Fixed matter	Residue on evaporation	110
	Deficiency in strength ...	Quantitative analysis	769
Liq. Ferri Dialysatus	General	Quantitative analysis	784
Liq. Ferri Acetatis Fortior ...	Ferrous salts	Ferricyanide of Potassium ...	180
Liq. Ferri Perchloridi Fortior	General impurity or deficiency	Specific gravity...	726
		Quantitative analysis	784
Liq. Ferri Pernit.	Arsenic (in the perchloride)	The copper test...	194
Liq. Ferri Persulphatis			
Liq. Hydrargyri Nitratis Acidus	Deficiency in strength ...	Specific gravity...	727
	Mercurous salts (nitrate) ...	Hydrochloric Acid	238
Liq. Lithiæ Efferves.	Gen. impur. or deficiency...	Quantitative analysis, etc. ...	260
Liq. Magnesiæ Carbonatis	Other Magnesian salts ...	Bitter taste ($MgCl_2$, $MgSO_4$)	132
	Gen. impur. or deficiency...	Quantitative analysis	781
Liq. Plumbi Subacetatis	General impurity or deficiency	Specific gravity	727
		Quantitative analysis	747
Liquor Potassæ ...	General impurity or deficiency	Specific gravity	727
		Quantitative analysis	746
	Carbonates	Effervescence with acids ...	370
		Lime-water...	370
	Calcium salts	Oxalate of Ammonium	128
	More than traces of Silica	Insol. in acid after evap., etc.	420
	Sulphates ...	Soluble barium salt, etc. ...	364
	Chlorides ...	Nitrate of Silver, etc.	311
	Alumina... ...	Ammonia to acid sol.	157
	Lead	Sulphuretted hydrogen	298
Liquor Potassæ Effervescens ...	Deficiency in strength ...	Quantitative analysis	746
	Bicarbonate of Sodium ...	Tartaric acid, etc.	777
Liquor Sodæ ...	General impurity or deficiency	Specific gravity...	726
		Quantitative analysis	746
	Calcium salts	Oxalate of Ammonium	128
	Carbonate (of Sodium)	Effervescence with acids... ...	369
		Lime-water...	369
	More than traces of Silica	Insol. in acids after evap., etc.	420
	Sulphates ...	Soluble barium salt, etc. ...	364
	Chlorides ...	Nitrate of Silver, etc.	311
	Alumina ...	Ammonia to acid sol.	157
	Lead	Sulphuretted Hydrogen	298
Liquor Sodæ Chlorinatæ.	Gen. impur. or deficiency	Quantitative analysis	770
	Calcium salts	Oxalate of Ammonium	128
Liq. Sodæ Efferves. ...	Deficiency in strength ...	Quantitative analysis	746

Name of Preparation.	Impurities.	Test.	Page.
Lithii Carbonas	Gen. impur. or deficiency	Quantitative analysis	261
	Calcium salts	Oxalate of Ammonium, etc.	128
	Alumina	Lime-water, etc.	117
Lithii Citras	Deficiency in strength	Quantitative analysis	261
Lupulinum	More than 15 per cent. ash	Incineration, etc.	510
	More than 40 per cent. insol. in ether	Digestion in Ether	510
Lycopodium	Starch, etc.	Microscope	565
	More than 5 per cent. of mineral matter	Incineration Earthy matter sinks in CS_2	110
Magnesia Levis Magnesia Ponderosa	Carbonate (of Magnesium)	Effervescence with acids	370
	Calcium (Hydrate or Carbonate)	Oxalate of Ammonium to acetic or other sol., etc.	128
	Sulphates (of Magnesium or Sodium).	Soluble barium salt, etc.	364
Magnesii Carbonas Levis Magnesii Carbonas Ponderosa	Alumina	Ammonia to acid solution	157
	Sulphates (of Magnesium or Sodium)	Soluble barium salt, etc.	364
	Calcium (Carbonate)	Oxalic Acid, etc.	128
	Iron, Lead, etc.	Sulph. Hydrogen to sol. in acid with excess of Ammonia	297
	Gen. impur. or deficiency	Quantitative analysis	781
Magnesii Sulphas	Calcium (Sulphate)	Oxalate of Ammonium	128
	Iron (Sulphate)	Chlorinated Lime or Soda	130
	General impurities	Quantitative analysis	781
Manna	Deficiency of Mannite	Quantitative analysis	554
Mel	More than 0·2 per cent. ash	Incineration	110
	More than trace of sulphates	Soluble barium salt, etc.	364
	Starch (flour)	Iodine	564
Morphinæ Acetas	Basic acetate	Quantitative analysis	822
Morphinæ Hydrochl.	General impurities	Quantitative analysis	821
Oleum Terebinthinæ	Petroleum Spirit	Distilling points, etc.	493
Opium	Deficiency in Morphine	Quantitative analysis	819
Paraldehydum	General	Melting- and boiling-point	578
	Acid	Neutrality	578
	Aldehyde	Alkali	578
	Sulphates, etc.	Soluble barium salt	365
	Chlorides	Nitrate of Silver	341
Phenacetinum	Mineral matter	Incineration	110
	Other Organic Matter	Sulphuric acid	Chars
	Acetanilide	Phenyl-isonitrile	649
Phenazonum	Mineral Matter	Incineration	110
	Acid	Neutrality	103
Picrotoxinum	Alkaloids	Mercuric Chloride, Platinic Chloride, Tannin	682
Plumbi Acetas	General	Quantitative analysis	747
Plumbi Carbonas	Sulphate of Lead or Barium or Silicates	Insolubility in Acetic acid 113, 246,	420
	Calcium (chalk)	Oxalate of Ammonium after removing Lead	277
Plumbi Oxidum	Carbonates	Effervescence with acids	369
	Copper (oxide)	Ammonia to acid solution	219
Potassa Caustica	More than traces of Chloride	Nitrate of Silver, etc.	311
	Sulphate	Soluble barium salt, etc.	364
	General impurities	Quantitative analysis	748
Potassa Sulphurata	Excess of Carbonate or Sulphate	More than 50 per cent. insoluble in spirit	70
Potassii Acetas	Iron, etc.	Sulphydrate of Ammonium	181
	Carbonate of Potassium	Effervescence with acids; alkalinity: insol. in spirit	369 71
Potassii Bicarbonas	General	Quantitative analysis	748

Name of Preparation.	Impurities.	Test.	Page.
Potassii Bromidum	Free Bromine	Odour	312
	Iodides	Chlorine-water and Starch	318
	General	Quantitative analysis	758
	Carbonates	Sacc. solution of Lime	369
	Sulphates	Soluble barium salt, etc.	364
	Bromates	Colour with dilute acid	346
Potassii Carbonas	More than traces of Silicate	Insol. acids after evap., etc.	420
	Sulphate	Soluble barium salt, etc.	364
	Chloride	Nitrate of Silver, etc.	311
	General	Quantitative analysis	748
Potassii Chloras	Chloride (of Potassium)	Nitrate of Silver, etc.	311
	Calcium (Chloride)	Oxalate of Ammonium	128
Potassii Citras	General	Quantitative analysis	749
Potassii Cyanidum	Iron	Ferrocyanide of Potassium	181
	Sulphates	Soluble barium salt, etc.	364
	General	Quantitative analysis	758
Potassii Ferricy.	Ferrocyanide	Ferric salt	181
Potassii Iodidum	Iodate (of Potassium)	Tartaric acid and Starch	79
	Chloride (of Potassium)	Nitrate of Silver, etc.	311
	Carbonate (of Potassium)	Sacc. solution of Lime	369
	General	Quantitative analysis	759
Potassii Nitras	Sulphate (of Potassium)	Soluble barium salt, etc.	364
	Chloride (of Potassium)	Nitrate of Silver, etc.	311
Potassii Permang.	General	Quantitative Analysis	768
Potassii Sulphas	Acid Sulphate of Potassium	Test-paper	103
	Calcium	Oxalate of Ammonium	128
Potassii Tartras Potassii Tart. Acida	General	Quantitative analysis	749
Quininæ Sulphas	Salicin	Sulphuric Acid	626
	General	Quantitative analysis	817
Rhei Radix	Turmeric	Boric Acid	394
Santoninum	Mineral Matter	Incineration	110
Sapo Durus	Earthy Soaps, etc.	Insolubility in spirit	549
	Oil	Oily stain to paper	549
	Potassium compounds	Deliquescence of ash	549
Sapo Mollis	Earthy Soaps, etc.	Insolubility in spirit	549
	Oil	Oily stain to paper	549
Scammoniæ Resina	Resin of Guaiacum	Potato-paring	549
	Resin of Jalap	Insolubility in ether	606
Scammonium	Carbonate (of Ca and Mg)	Effervescence with acids	369
	Starch (flour)	Solution of Iodine	564
	General impurities	Quantitative analysis	606
Sinapis	Starch (flour)	Solution of Iodine	564
Soda Caustica	More than traces of Chloride	Nitrate of Silver, etc.	311
	Sulphate	Soluble barium salt, etc.	364
	General impurities	Quantitative analysis	748
Soda Tartarata	General	Quantitative analysis	749
Sodii Arsenias	Excess or deficiency of water of crystallization.	Quantitative analysis	785
	General		
Sodii Benzoas	General	Quantitative analysis	750
Sodii Bicarbonas	Neutral Carbonate	Mercuric Chloride	239
	More than traces of Chlorides	Nitrate of Silver, etc.	311
	Sulphates	Soluble barium salt, etc.	364
	General	Quantitative analysis	748
Sodii Bromidum	Iodides	Chlorine and Starch	318
	General	Quantitative analysis	748
Sodii Carbonas	Excess or deficiency of water of cryst., etc.	Quantitative analysis	748
	More than traces of Chlorides	Nitrate of Silver, etc.	311
	Sulphates	Soluble barium salt	364
Sodii Hyposulphis	General	Quantitative analysis	763

Name of Preparation.	Impurities.	Test.	Page.
Sodii Hypophosphis	Carbonates	Effervescence with acid	369
	Phosphates or Phosphites	Acetate of Lead	407
	Calcium	Oxalate of Ammonium	128
	General	Permanganate of Potassium ...	408
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	Chlorides	Nitrate of Silver, etc.	311
	Carbonates	Sacc. solution of Lime	369
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	Sulphate (of Sodium) ...	Soluble barium salt, etc. ...	364
Sodii Nitris	More than 5 per cent. ...	Quantitative analysis	415
	Oxalates	Chloride of Calcium	372
Sodii Phosphas ...	More than trace of Sulphate	Soluble barium salt, etc.... ...	364
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Spiritus Chloroformi	General	Specific gravity...	726
Spiritus Rectificatus	General (excess of water)...	Specific gravity...	726
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Veratrina	Mineral matter	Incineration	110
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	Copper (Acetate)...	Ammonia	219
Zinci Carbonas ...	Sulphates	Soluble barium salt, etc. ..	364
	Chlorides	Nitrate of Silver, etc.	311
	Copper (Carbonate)	Ammonia to acid solution ...	219

Name of Preparation.	Impurities.	Test.	Page.
Zinci Chloridum ...	Metals (As, Cd, Cu, Pb) ...	Sulphuretted Hydrogen... ...	298
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	Ferrous salts (Chloride) ...	Ferricyanide of Potassium ..	180
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	Sulphates (Sodium or Zinc)	Soluble barium salt, etc. ...	364
	Chlorides	Nitrate of Silver, etc.	311
	Copper (Oxide)	Ammonia to acid solution ...	219
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		Nitric Acid ; Ammonia	181
	Copper (Sulphate)	Ammonia	219
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SATURATION TABLES.

Equivalent weights of Citric Acid, Tartaric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, Carbonate of Ammonium, and Carbonate of Magnesium; repeated (in black) for 20 parts of each, and incidentally (in roman) for other proportions. (Exact to two places of decimals.)

Citric Acid ($H_3C_6H_5O_7$, H_2O) $\div 3 \times 2 = 140$	**20·00**	18·66	**16·96**	**14·00**	**9·78**	**16·66**	**26·74**	**29·31**
Tartaric Acid $H_2C_4H_4O_6 = 150$	21·43	**20·00**	**18·26**	**15·00**	**10·49**	**17·85**	**28·65**	**31·41**
Carbonate of Potassium $K_2CO_3 + 16\%$ Aq $= 164·285$	**23·47**	**21·90**	**20·00**	16·43	11·48	19·52	31·38	34·40
Bicarbonate of Potassium $2(KHCO_3) = 200$	**28·57**	**26·66**	24·34	**20·00**	13·98	23·81	38·20	41·90
Carbonate of Sodium Na_2CO_3, $10H_2O = 286$	**40·86**	**38·13**	34·81	28·60	**20·00**	34·04	54·63	59·98
Bicarbonate of Sodium $2(NaHCO_3) = 168$	**24·00**	**22·40**	20·45	16·80	11·74	**20·00**	32·09	35·18
Carbonate of Ammonium $(N_3H_{11}C_2O_5) \div 3 \times 2 = 104·7$	**14·96**	**13·95**	12·68	10·47	7·31	12·46	**20·00**	21·86
Carb. of Magnes. $((MgCO_3)_3$, $Mg2HO$, $4H_2O) \div 4 = 95·5$	**13·64**	**12·73**	11·62	9·55	6·68	11·37	18·24	**20·00**

The amount of acid given in any column will saturate the amount of carbonate in the same column, and *vice versâ.*
The amounts of carbonate in any column are equal to each other in chemical power.
Lemon-Juice (sp. gr. 1·040) contains, on an average, 9 per cent. by weight of citric acid.

The same Table in round numbers, for purposes of prescribing and dispensing.

Citric Acid	**20**	19	**17**	**14**	**10**	**17**	**27**	**30**
Tartaric Acid	22	**20**	**18**	**15**	**11**	**18**	**29**	**32**
Carbonate of Potassium (Potassii Carbonas, B.P.)	**24**	**22**	**20**	16	12	20	31	35
Bicarbonate of Potassium (Potassii Bicarbonas, B.P.)	**29**	**27**	24	**20**	14	24	38	42
Carbonate of Sodium (cryst.) (Sodii Carbonas, B.P.)	**41**	**38**	34	28	**20**	34	55	60
Bicarbonate of Sodium (Sodii Bicarbonas, B.P.)	**24**	**22**	20	17	12	**20**	32	36
Carbonate of Ammonium (Ammonii Carbonas, B.P.)	**15**	**14**	13	11	7	13	**20**	22
Carbonate of Magnesium (Magnesii Carbonas, B.P.)	**13**	**13**	11	9	7	11	18	**20**

The Table is read thus:—20 grains of Citric Acid will saturate 29 grains of Bicarbonate of Potassium; 20 grains of Bicarbonate of Sodium will saturate, or be saturated by, 18 grains of Tartaric Acid; 11 grains of Tartaric Acid=7 grains of Carbonate of Ammonium; 20 grains of Bicarbonate of Sodium are equivalent to, or will do as much work as, 34 grains of Carbonate of Sodium; 14 grains of Citric Acid are as strong as 15 of Tartaric Acid. It is occasionally convenient to double the numbers, halve them, or take some other proportion; also to employ them in weights other than grains.

Lemon-Juice contains on an average, 41 grains of Citric Acid in 1 fluid ounce, or 5 grains per fluid drachm.

THE ELEMENTS.

	Symbol and Atomic Value.	Atomic Weight.
Aluminium (Al_2^{VI})	Al^{IV}	27
Antimony (Sb^{III})	Sb^{V}	120
Arsenium (As^{III}) (74·9, Kessler)	As^{V}	75
Barium (136·84, Marignac; 137·12 if O=16)	Ba^{II}	136·8
Beryllium (or Glucinum) (9·3, Awdejew; Klatzo)	Be^{II}	9·1
Bismuth (Bi^{III}) (210, Dumas; 207·5, if O=15·96)	Bi^{V}	208
Boron (10·9, Berzelius; 10·97, Clarke)	B^{III}	11
Bromine (79·75, Stas; 79·96, if O=16)	Br^{I}	80
Cadmium (111·7, Lenssen)	Cd^{II}	112
Cæsium (132·7, Johnson & Allen, Bunsen; 133, if O=16)	Cs^{I}	133
Calcium (39·9, Erdmann and Marchand; 40, if O=16)	Ca^{II}	40
Carbon (C^{II})	C^{IV}	12
Cerium (Ce^{III}) (138, Mendelejeff)	Ce^{VI}	141·5
Chlorine (35·368, Stas) 35·4, if O=16	Cl^{I}	35·5
Chromium (Cr_2^{VI}) (52·08, Siewert)	Cr^{VI}	52·5
Cobalt (Co^{II})	Co^{VI}	58·6
Copper (63·12, Millon & Commaille; 63·3, if O=16)	Cu^{II}	63·3
Didymium (?)	D^{II}	145
Erbium (?)	Eb^{III}	166
Fluorine (18·96, Luca, Louyet)	F^{I}	19
Germanium (72·3, Boisbaudran)	—	—
Gallium	Ga	70
Glucinum, *see* Beryllium	—	—
Gold (Au^{I}) (196·2, Berzelius; 196·64, Kruss; 196·85, Thorpe and Laurie)	Au^{III}	197
Hydrogen (1·0025 if O=16)	H^{I}	1
Indium	In^{VI}	113·7
Iodine (126·533, Stas; 126·86, if O=16)	I^{I}	127
Iridium	Ir^{IV}	193
Iron (Fe^{II} & Fe_2^{VI}) (55·9, Dumas)	Fe^{VI}	56
Lanthanium (138·85, Clarke, Moyer and Seubert)	La^{III}	138
Lead (Pb^{II}) (206·9, Stas)	Pb^{IV}	206·4
Lithium	L^{I}	7
Magnesium (24·4, Van der Plaats, Ostwald)	Mg^{II}	24
Manganese (Mn^{II} & Mn^{IV}) (54·8, Dewar & Scott)	Mn^{VI}	55
Mercury (199·8, Erdmann & Marchand; 200·1 to 200·4, others)	Hg^{II}	200
Molybdenum (95·9, Dumas; Debray)	Mo^{VI}	96
Nickel (Ni^{II})	Ni^{VI}	58·6
Niobium	Nb^{V}	94
Nitrogen (N^{I} & N^{III}) (14·009, Stas; 14·04, if O=16)	N^{V}	14
Osmium (200, Ostwald)	Os^{IV}	195
Oxygen (15·96 Stas, Nilson)	O^{II}	16

THE ELEMENTS (*continued*).

	Symbol and Atomic Value.	Atomic Weight.
Palladium	Pd^{IV}	106·2
Phosphorus (P^{III}) (30·96, Schrötter)	P^{V}	31
Platinum (194·9, if O = 16)	Pt^{IV}	194·4
Potassium (39·04 Stas ; 39·1, if O = 16)	K^{I}	39
Rhodium (104·1, Berzelius)	Rh^{IV}	104·3
Rubidium (85·2, Bunsen)	Rb^{I}	85·4
Ruthenium (103·5, Berzelius)	Ru^{IV}	104·2
Scandium	Sc	44
Selenium (or Selenion) (79, various observers)	Se^{IV}	78·9
Silicon (28·3, Clarke)	Si^{IV}	28
Silver (107·66 Stas ; 107·93, if O = 16)	Ag^{I}	108
Sodium (22·98 Stas ; 23·05, if O = 16)	Na^{I}	23
Strontium (87·3 if H = 1)	Sr^{II}	87·5
Sulphur (S^{II} & S^{IV})	S^{VI}	32
Tantalum (182·8, Van der Plaats, Ostwald)	Ta^{V}	182
Tellurium (128, Meyer and Seubert)	Te^{VI}	125
Thallium (203·5, Crookes)	Tl^{III}	204
Thorinum (or Thorium) (234, Clarke)	Th^{II}	233
Tin (Sn^{II}) (117·4, Dumas ; 117·97, Clarke)	Sn^{IV}	118
Titanium (50, Clarke)	Ti^{IV}	48
Tungsten (183·6, if H = 1)	W^{VI}	184
Uranium (239·8, Ebelmen)	U^{VI}	240
Vanadium (51·37, Clarke)	V^{V}	51
Ytterbium	Yb	173
Yttrium (89, Ostwald)	Y^{III}	90
Zinc (64·7, Axel Erdmann ; 65·4, Ostwald)	Zn^{II}	64·9
Zirconium (89·57, Clarke ; 90·7, Ostwald)	Zr^{IV}	90·4

The quantivalence or atomic value (for combination or exchange) of some elements is, apparently, variable: in the above Table the full coefficients are given in the column of symbols, other common values in brackets.

Atomic weights were somewhat obscurely termed *equivalents* by Wollaston.

Other elements than the above exist. They are very rare. Some of the rarer so-called elements may not be truly elementary.

Note. Students must expect the figures representing the atomic weights of elements to vary slightly from time to time, in accordance with the advancement of knowledge in the directions of purity of materials and improvements in manipulation, and as regards modes of research and realization of chemical and physical analogies amongst elements. Atomic weights have also been founded, at different times, on different units, or starting points, namely: H = 1 and O = 16; H = 1 and O = 15·96; and O = 16 and H = 1·0025. In the foregoing table the atomic weights in large figures are those which, as a rule, at present will be found more useful to English medical and pharmaceutical workers. See a suggestive paper, with lists, by Venables, in the *Chemical News*, vol. lix. pp. 77 and 89: from the *Journal of the Elisha Mitchell Scientific Society*, vol. v., part 2.

[*For* ERRATA *see the last page of the Index.*]

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